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THE INFLUENCE OF THE PHYSICAL PROPERTIES OF SODIUM SOAPS ON THEIR DISPERSIONS IN MINERAL OIL[1]

BY F. W. SOUTHAM[2] AND I. E. PUDDINGTON[2]

Abstract

The densities of the anhydrous sodium salts of the fatty acids from caproic to stearic have been measured over a temperature range of 30° to 300° C. and the results obtained correlated with the properties of lyophilic dispersions of sodium soaps in mineral oil.

Introduction

The conventional method of preparing stable lyophilic dispersions of saturated sodium soaps in mineral oils involves heating the soap, or the soap containing a limited amount of oil, to a temperature of about 160° C., and adding the remainder of the oil slowly and with constant stirring as the temperature of the dispersion is gradually reduced to 120° C. If the agitation is such that the system is subjected to high shearing stresses, the maximum temperature may then be reduced to about 120° C. and the total quantity of soap and oil may be treated at one time (2). Further reduction in the temperature, however, prior to the application of high shear produces an unstable dispersion in which the soap appears to be completely lyophobic. This sudden change from the lyophobic to the lyophilic system, which takes place within a short temperature interval, is of considerable interest, since a large density change in the soap occurs at about the same temperature, and could be associated with it.

Following the terminology of Thiessen (4, 5), who suggested "unidimensional melting" for the change in state that is found in a soap at the melting point of the corresponding fatty acid, bidimensional melting has been suggested as the cause of this second density change (1). Here, presumably, the soap crystal has absorbed enough thermal energy for the hydrocarbon chains to separate sufficiently for oil to penetrate the crystal lattice, and, at the same time, the soap becomes plastic. This penetration of oil is greatly assisted by shearing the crystal, and by the proper control of temperature and shearing forces, soap micelles of predetermined size, shape, and stability can be produced (2).

When the number of carbon atoms in the soap molecule has been reduced below eight, it is well known industrially that it is no longer possible to prepare

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[2] *Chemist.*

stable dispersions by the conventional method. If the proposed explanation for the formation of the lyophilic soap micelles is correct, changes in state of the sodium soap crystal with temperature should show a discontinuity as the size of the molecule is reduced below eight carbon atoms. In view of this it was decided to investigate the density–temperature changes of the sodium soaps of the fatty acids on both sides of the critical eight carbon atom chain length. Results are reported from caproic to stearic.

Experimental

The stearic acid used in this work was laboratory prepared from a technical sample by the method of Philipson, Heldman, Lyon, and Vold (3) and had a melting point of 68.3° C. Palmitic, capric, and caproic acids were supplied by Eastman Kodak Co., myristic by City Chemical Corporation, and lauric and caprylic by the Paragon Testing Laboratories. The soaps were prepared by titrating an alcoholic solution of the acid with alcoholic sodium hydroxide, using phenolphthalein as an external indicator. The soap was then recovered by evaporation of the solvents.

In making the density determination, about 1.5 gm. of soap powder was melted *in vacuo* to remove the last traces of water and solvent. After cooling in an atmosphere of nitrogen, the cake of solid soap was removed and its density determined by a mercury displacement method.

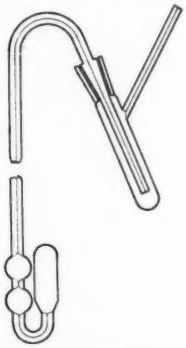

FIG. 1. *Form of dilatometer used.*

The dilatometers were of the form shown in Fig. 1 and were constructed and filled as follows. The soap block was placed in a sealed-off tube of slightly larger diameter, which was then drawn down and sealed to a 30 cm. length of capillary. The male member of a capillary bore ground glass joint, to which about 6 cm. of fine capillary had been sealed, was then attached, and the dilatometer completed by bending in the form shown in Fig. 1. Filling with mercury was accomplished by attaching the ground glass joint to a vacuum system and reducing the pressure to about 10^{-4} mm. of mercury, after which the mercury was forced into the dilatometer under atmospheric pressure.

The dilatometer bulbs were placed in an air thermostat, the temperature of which could be controlled to ± 0.2° C. A weighing bottle, containing sufficient mercury to cover the tip of the capillary, was then attached to the ground glass joint, and the mercury displaced from the dilatometer by the expanding soap could be determined precisely. A capillary vent in the weighing bottle prevented any loss of the mercury by evaporation during the experiments.

Results

Fig. 2 shows the results obtained with the soaps investigated. Increments of density rather than the absolute figures are shown on the graph in order to separate the curves. The actual densities found at 27.0° C. are given in Table I.

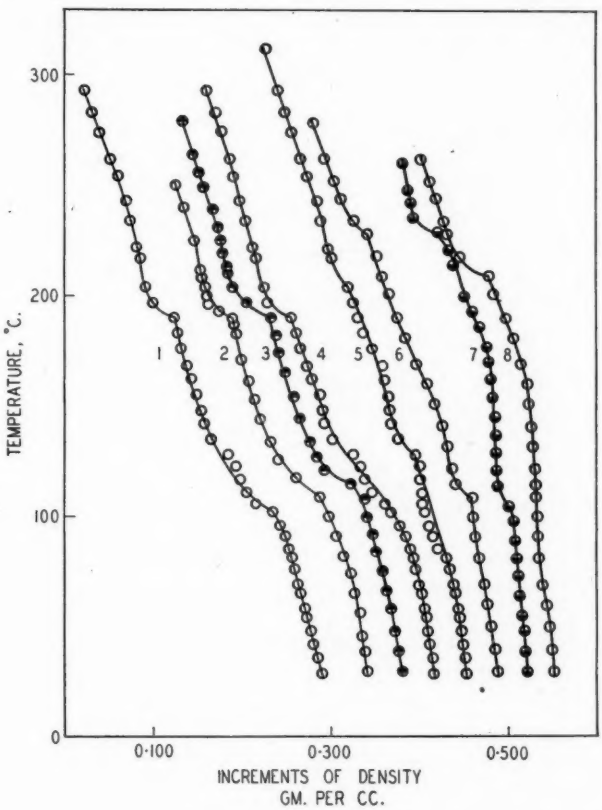

FIG. 2. *Density–temperature relations for anhydrous sodium soaps. Curves 1 to 8 represent respectively the relations for the sodium salts of stearic (technical), stearic, palmitic, myristic, lauric, capric, caprylic, and caproic acids.*

TABLE I

DENSITIES OF ANHYDROUS SODIUM SOAPS

Stearate, pure	1.103	Laurate	1.150
Stearate, technical	1.088	Caprate	1.172
Palmitate	1.111	Caprylate	1.214
Myristate	1.133	Caproate	1.264

The curves shown are in substantial agreement with the qualitative data presented by Vold, Macomber, and Vold (6), and the usual large changes in density are shown at 100° to 120°, and 190° C. in the case of the higher molecular weight fatty acids, the latter density break occurring at higher temperatures as the chain length of the fatty acid is reduced. No substantial difference can be noted between the samples of pure and technical grades of sodium stearate. The bidimensional melting point, which is shown by all the soaps down to and including sodium caprylate, is entirely absent in the case of the caproate. The rather large increase in density in this vicinity indicated by Vold and co-workers (6) for the caprate was not found; its behaviour appeared to be in line with that of the higher members of the series.

The absence of bidimensional melting in sodium caproate suggests that the non-polar bonds between the adjacent hydrocarbon chains become approximately as strong as the polar bonds between the sodium carboxyl groups when the carbon chain length is sufficiently reduced, and only one melting point will occur. This is borne out by the fact that only one break is found in the density curve, at 210° C., for the soap containing six carbon atoms. The theory that the formation of lyophilic dispersions of sodium soaps in mineral oil by a comminution process is dependent on the existence of bidimensional melting in the anhydrous soap is thus in agreement with the experimental facts, since only those soaps possessing it are capable of forming stable dispersions.

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THE FLOW PROPERTIES OF SOME ANHYDROUS SODIUM SOAPS[1]

By F. W. Southam[2] and I. E. Puddington[2]

Abstract

The flow properties of anhydrous sodium stearate have been followed in some detail over the temperature range 45° to 140° C., using an extrusion plastometer. Comparative results have been obtained at a single temperature with the sodium soaps of some of the lower fatty acids. The results indicate large changes in the properties of sodium stearate at 68° and 105° C. An abrupt change is also observed when the number of carbon atoms in the soap is reduced below eight.

Introduction

Previous publications have demonstrated several changes of state in the sodium soaps of the higher fatty acids as they are heated from room temperature to the melting point. For example, dilatometric measurements over this temperature range show two gross irregularities in the density–temperature curve at about 105° to 120° C. and 200° C., with minor breaks at other temperatures (1, 3, 6).

A change in the state of dispersion of aqueous soap solutions at the melting point of the fatty acid used in preparing the soap, noted years ago by Kraft, formed the subject for several papers by Thiessen and co-workers (4, 5). They noted irregularities in the specific volume, dielectric constant, optical double refraction, and specific heats of the soaps at this temperature, as well as a broadening in the interference representing the larger spacing at right angles to the axis of the soap crystal. From the changes so observed, Thiessen concluded that the soap underwent partial melting at this point; that is, sufficient thermal energy had been provided to bring about a loosening of the crystal lattice in one dimension. A similar explanation has been suggested to account for the larger density change at 105° to 120° C. (1). If these postulates are correct, the flow properties of the soaps should show marked changes at these points, and an investigation into this phase of their behaviour might be expected to make worth while contributions to our knowledge of the nature of soaps.

When a solid material is completely melted, the changes in its flow properties are too great to be conveniently followed by means of a single instrument, and the material for the present paper is confined to the results obtained in a preliminary investigation of several soaps in the temperature range of 45° to 140° C.

[1] *Manuscript received October 28, 1946.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1508.

[2] *Chemist.*

Experimental

The soap samples used were a part of those employed in another investigation; their preparation and properties have been described (3). Changes in flow properties were followed with an extrusion plastometer similar to the one described by Gallay and Tapp (2). The extrusion capillary was 0.0109 cm. in diameter and 0.66 cm. in length. Pressure was applied to the plastometer with a manually controlled, 10 ton, Carver laboratory press. The pressure was measured by means of a special gauge inserted between the plastometer and the top platen of the press. It consisted of a lapped piston and cylinder, of 0.5 sq. in. cross-sectional area, filled with S.A.E. No. 60 oil; an indicating pressure gauge was coupled directly to the oil chamber. The gauge was calibrated with known weights before use. Pressures on the soap could be maintained within ± 33 lb. per sq. in. The temperature of the plastometer was controlled to ± 0.5° C. with an air thermostat.

Soap blocks, previously melted *in vacuo* to remove traces of water, were moulded to the correct size before inserting into the plastometer. One and one-half hours was allowed for the temperature of the sample to reach equilibrium before readings were taken, and several feet of the soap were extruded

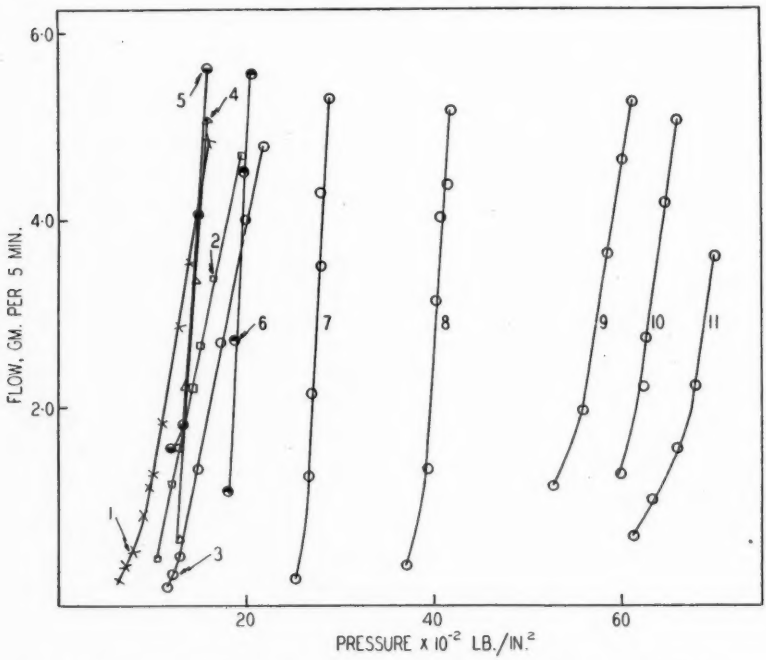

FIG. 1. *Flow–pressure relations for pure sodium stearate. Curves 1 to 11 represent respectively results obtained at 140°, 130°, 120°, 110°, 100°, 95°, 85°, 70°, 65°, 60°, and 55° C.*

before the thread was cut off flush with the capillary, and the amount flowing in five minutes noted by weighing.

Results

Fig. 1 shows the behaviour of pure sodium stearate when the rates of flow at various pressures are observed over a temperature range. Fig. 2, included for comparison, shows similar results for technical sodium stearate.

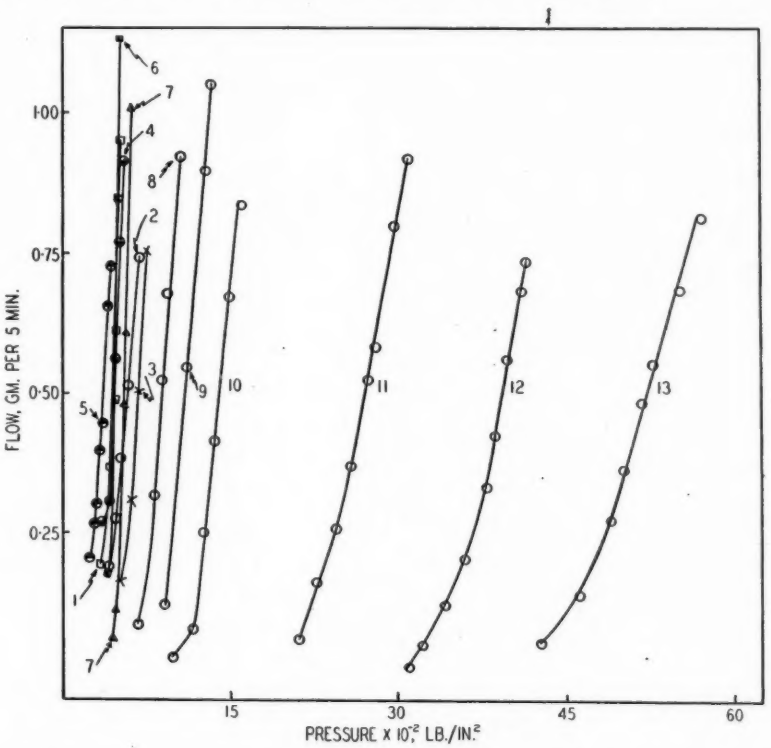

FIG. 2. *Flow–pressure relations for technical sodium stearate. Curves 1 to 13 represent respectively results obtained at 140°, 130°, 125°, 115°, 110°, 100°, 90°, 75°, 65°, 60°, 55°, 50°, and 45° C.*

In the case of the pure soap, large changes in the slopes of the curves may be noted between 100° and 110° C. and between 65° and 70° C., while the deviations in the curves representing the technical soap are at somewhat different temperatures and are not so pronounced. This is not surprising since the technical material contains a mixture of fatty acids (m.p., 52° to 55° C. compared to 68.5° C. for pure stearic), which would be expected to mask the behaviour of a single pure acid.

Figs. 3 and 4 supplement Figs. 1 and 2 and show respectively the variation of mobility and yield value (the extrapolated intercept of the pressure axis at zero flow) with temperature. These graphs accentuate the discontinuities noted in Figs. 1 and 2, both showing marked breaks at the melting point of the fatty acid and in the vicinity of 110° C.

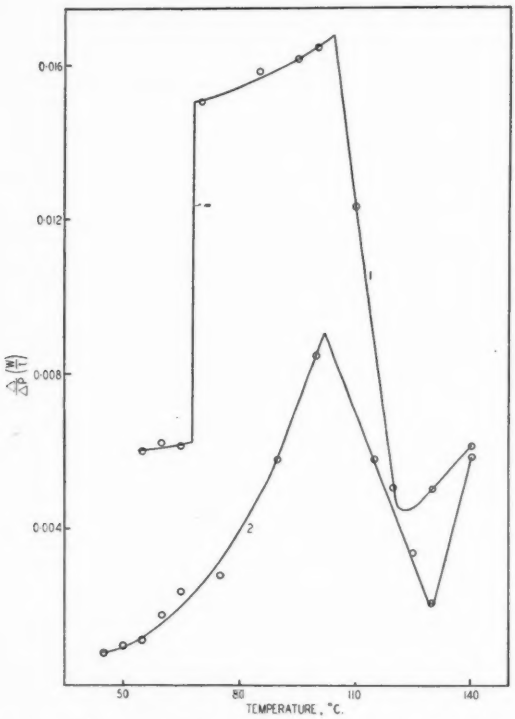

FIG. 3. *Change in mobility with temperature. 1, pure sodium stearate; 2, technical sodium stearate.*

It should be noted here that the pressure figures quoted are not corrected and are therefore not independent of the capillary dimensions. Rates of flow have also been reported as masses rather than volumes. The irregularities noted in the flow properties, however, are so large that the change in units has little effect on the general shape of the curves.

In Fig. 5 the change in yield value per carbon atom is plotted against the number of carbon atoms in the molecule. The marked increase in yield value as the number of carbon atoms is reduced from eight to six is obvious. These values were obtained from flow–pressure curves of the different soaps at 140° C.

A few experiments, carried out without melting the soap *in vacuo* to ensure the complete removal of water, indicated that traces of moisture had little

effect on the flow properties below 100° C.; above this temperature the effect was to increase the rate of flow at any pressure.

Discussion

Thiessen's postulate, that the soap undergoes partial melting at the melting point of the fatty acid from which it is prepared, appears to receive support from the present work, since a marked decrease in yield value and a tremendous

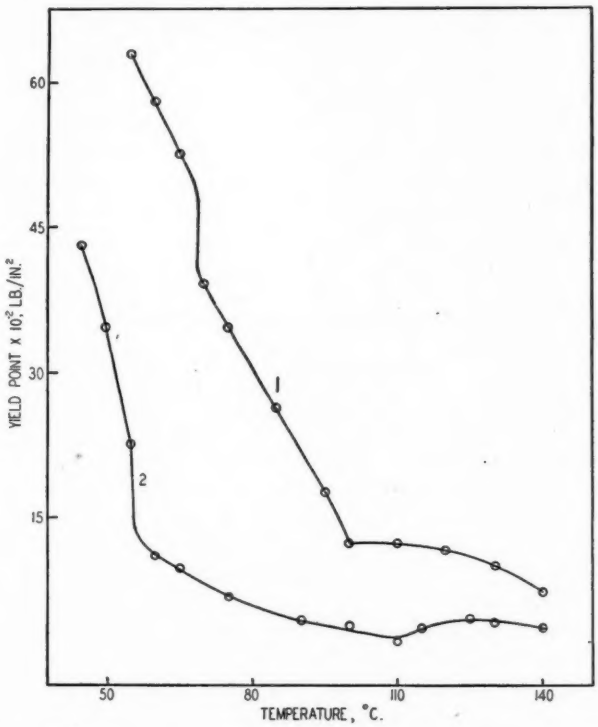

FIG. 4. *Change in yield value with temperature. 1, pure sodium stearate; 2, technical sodium stearate.*

increase in mobility occur at this point. Both of these changes would be expected with the loosening of the crystal bonds in one dimension and the consequent provision of easier slip planes. Qualitatively, a change was noted in the appearance of the extruded soap; below 68° C. it tended to crumble easily, while above this point it was much more coherent.

As the temperature is increased over a further 40° C. interval, the yield value continues to fall in a linear manner. This thermal weakening of the soap crystal continues until a temperature of about 105° C. is reached; after

which the yield value falls off at a greatly reduced rate over the remaining temperature interval examined. This point, 105° C., would appear to indicate complete disruption of another crystal bond which had a strength not greatly different from that broken at 68° C., since the rates of falling-off

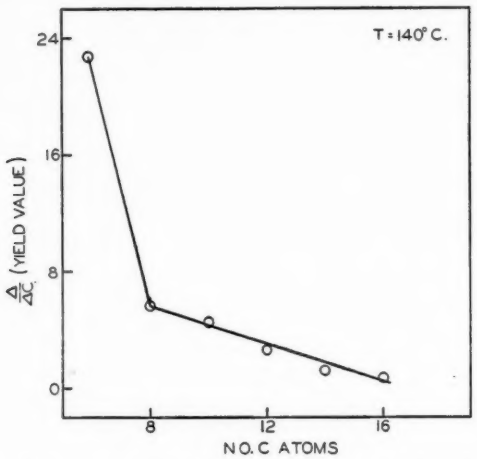

FIG. 5. *Rate of change of yield value with the number of carbon atoms in pure sodium soaps.*

in the yield point with increased temperature were virtually identical above and below the unidimensional melting point. The much more gradual falling-off in yield point above 105° C. indicates much stronger remaining crystal forces. Since the soap molecule is distinctly heteropolar, much stronger bonds exist between the highly polar sodium carboxylic groups than between the non-polar hydrocarbon chains in the crystal lattice, and such behaviour is not unexpected. The behaviour of the technical sample is essentially the same as that of the pure soap, due allowance being made for its heterogeneous nature.

An alternative explanation might be based on the findings of Vold *et al.* (6), who reported the appearance of new soap phases at 90°, 117°, and 132° C. Since only one substantial change in flow properties has been found, however, that does not coincide with any of the temperatures noted by Vold, such an explanation does not appear to be valid.

Changes in the mobility of the soap with temperature, shown in Fig. 4, are also of considerable interest. In the temperature intervals 45° to 65° C. and 70° to 100° C. the mobility is approximately constant with the expected large increase in the 65° to 70° C. range. The large and abrupt fall at 105° C. followed by a slight rise is somewhat unexpected. However, this can be explained on the basis of the following considerations. When the soap crystal has undergone unidimensional melting, slip planes are afforded that offer

little resistance to flow once the yield value has been exceeded. When the second set of crystal bonds are broken, however, considerable resistance to flow is set up by the interference of the long molecular chains, and more work will have to be done to push them past each other than before the bidimensional melting. That this is the case may be seen on a macroscale. Below 110° C. the soap is quite brittle while at higher temperatures it is rather plastic and can be drawn out into long fibres. This increased cohesion and fibre forming property are doubtless due to the mutual interference of groups of molecules. The gradual weakening of the remaining crystal lattice forces will account for the slow increase in mobility after the initial large decrease.

Fig. 5 indicates the increasing strength of the non-polar crystal bonds as the hydrocarbon chain is shortened. The decided increase in the rate of change of yield point per carbon atom between eight and six carbon atoms shows a very marked increase in bond strength in this region. This is in perfect agreement with dilatometric results, where it was found that, while a soap with eight carbon atoms showed the usual large break in the density–temperature curve, indicating bidimensional melting, this portion of the curve was completely linear in the case of the soap containing six carbon atoms. It also bears out the observations of grease makers, that it is not possible to prepare greases in the usual way using soda soaps containing fewer than eight carbon atoms.

Acknowledgment

The valuable technical assistance rendered by R. Farnand and R. Schnarr during the course of this work is gratefully acknowledged.

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A NOTE ON THE USE OF MULTI-TIP ELECTRODES IN POLAROGRAPHIC WORK[1]

By J. McGilvery,[2] R. C. Hawkings,[3] and H. G. Thode[4]

Abstract

In the past, a dropping mercury electrode for polarographic work has consisted of a single capillary dipping in a solution. We have used two or more capillaries in parallel to increase cathode surface and thereby increase the diffusion current and the sensitivity of the instrument. The results indicate that each tip gives a diffusion current proportional to its calibration constant and that multi-tip electrodes give diffusion currents proportional to the sum of the capillary constants. Further, galvanometer oscillations are reduced considerably by the use of multi-tip electrodes. The use of multi-tip electrodes, therefore, makes it possible to extend the limits of detection and provides a means for reducing objectionable galvanometer oscillations.

During the war, polarographic procedures were developed for the determination of trace elements in metals and alloys (1, 2). In the course of this work, a capillary was found with two parallel bores. This chance use of a double-tip electrode led to a general study of multi-tip electrodes, with the view of extending the detection limits of the polarograph and improving on its accuracy. It was found that each tip gave a diffusion current proportional to its calibration constant, and that a five-tip electrode gave a diffusion current proportional to the sum of the five capillary constants. In view of the need for more sensitive analytical methods, it seemed desirable to report briefly on our use of multi-tip electrodes.

The average diffusion current during the life of a mercury drop is given by the 'Ilkovic equation', which can be expressed as follows:

$$\bar{i}_d = 605\, n\, D^{1/2}\, C\, m^{2/3}\, t^{1/6},$$

where n is the number of faradays of electricity required per mole of electrode reaction,

D is the diffusion coefficient in units cm.^{2} sec.$^{-1}$,

C is the concentration of the reducible material in terms of moles per cc.,

m is the rate of flow of mercury from the capillary in gm. sec.$^{-1}$, and

t is the drop time of the capillary in sec.

The factors determining the magnitude of the diffusion current may be separated into two main groups: those dependent on the solution n, D, and C, and those inherent in the apparatus, m and t. The use of multi-tip electrodes makes it possible to increase the factor $m^{2/3}\, t^{1/6}$ and still have t of suitable magnitude for polarographic work. The method is simply to connect two

[1] *Manuscript received January 6, 1947.*
Contribution from McMaster University, Hamilton, Ont.

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[3] *Graduate student; now at Northwestern University, Evanston, Ill., U.S.A.*
[4] *Professor of Chemistry.*

or more capillaries in parallel with the mercury drops from each flowing into the same solution. In this way, each capillary or tip acts as a separate cathode, and each should give rise to a diffusion current proportional to its $m^{2/3}\,t^{1/6}$ factor. The total diffusion current should, therefore, be proportional to the sum of these factors for the different tips.

The results reported below were obtained with a Sargent Model XI Polarograph using penta-tip electrodes.

Results and Discussion

Fig. 1 shows typical Cd^{++} waves obtained with a 5×10^{-6} molar solution of cadmium nitrate. The average height of the Cd^{++} waves was found to be 8.6 ± 0.3 cm. for the six curves reproduced on a reduced scale in Fig. 1. Actually, the average wave height obtained for a large number of determinations made with three different test solutions is in agreement with this value.

The $m^{2/3}t^{1/6}$ factor was determined for each of the five capillaries used in the penta-tip electrode. The sum of these factors for the five capillaries was found to be 16.2 mgm.$^{2/3}$ sec.$^{1/2}$. Substitution of this value in the 'Ilkovic equation' gives an average diffusion current of 0.264 μamp. for the above solution (5×10^{-6} M cadmium nitrate) or an equivalent wave height of 8.8 cm. This is in good agreement with the wave height found.

The results of determinations made with cadmium nitrate solutions ranging in concentration from 5×10^{-6} to 1×10^{-7} using a penta-tip electrode are given in Table I.

TABLE I

Cd^{++} WAVES OBTAINED WITH PENTA-TIP ELECTRODE

Supporting electrolyte: 0.1 molar potassium chloride; 0.1% gelatin. Temp., 25° C.

Concentration of $Cd(NO_3)_2$ solution, moles/litre	Wave height, cm.	Ratio of wave height to concentration
5×10^{-6}	10.4	2.7×10^{6}
1×10^{-6}	2.7	2.1×10^{6}
7.5×10^{-7}	2.7	3.6×10^{6}
5×10^{-7}	2.1	4.2×10^{6}
1×10^{-7}	No wave	

Because of high residual currents, it was not possible to detect the Cd^{++} wave for the 10^{-7} M cadmium nitrate solution. However, it may be possible to overcome this difficulty by using suitable compensating resistances and perhaps by lowering the pressure head of mercury and thereby increasing drop time.

Finally, it was found that galvanometer oscillations are reduced considerably by the use of multi-tip electrodes. Since the drops falling from the different

tips are out of phase, these unwanted oscillations, which are most serious when operating at high sensitivity, are considerably reduced. The same effect has been achieved by condenser damping (3, pp. 231-233). However, with the multi-tips there is the added advantage of increased sensitivity.

The use of multi-tip electrodes, therefore, makes it possible to extend the limits of detection by the polarographic method, and provides a means for reducing objectionable galvanometer oscillations.

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PLATE I

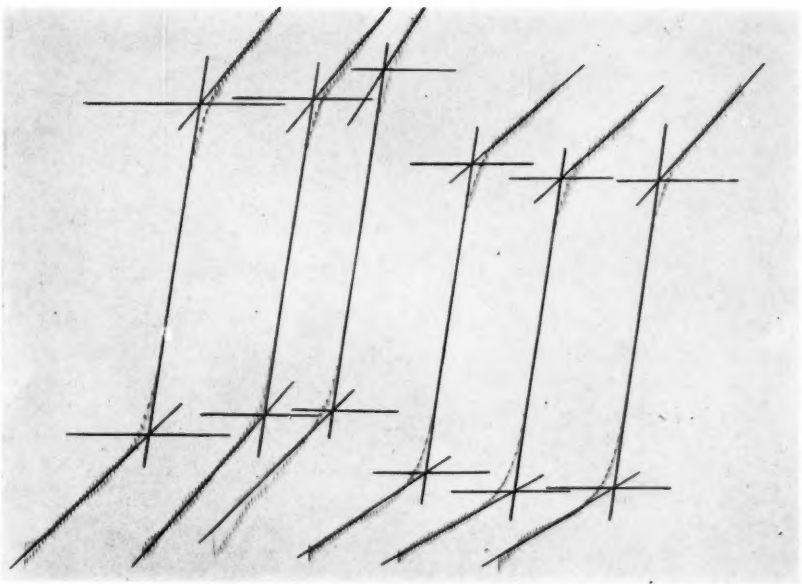

FIG. 1. *Typical Cd^{++} waves obtained for a 5×10^{-6} M solution using a penta-tip electrode.*

THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE VAPOUR. II.[1]

By Paul A. Giguère[2]

Abstract

The decomposition of hydrogen peroxide vapour has been investigated at low pressures (5 to 6 mm.) in the temperature range 50° to 420° C., for the purpose of determining the effect of the nature and treatment of the active surfaces. The reaction was followed in an all-glass apparatus and, except in one case, with one-litre round flasks as reaction vessels. Soft glass, Pyrex, quartz, and metallized surfaces variously treated were used. In most cases the decomposition was found to be mainly of the first order but the rates varied markedly from one vessel to another, even with vessels made of the same type of glass. On a quartz surface the decomposition was preceded by an induction period at low temperatures. Fusing the glass vessels slowed the reaction considerably and increased its apparent activation energy; this effect was destroyed by acid washing. Attempts to poison the surface with hydrocyanic acid gave no noticeable result. The marked importance of surface effects at all temperatures is considered as an indication that the reaction was predominantly heterogeneous under the prevailing conditions. Values ranging from 8 to 20 kcal. were found for the apparent energy of activation. It is concluded that the decomposition of hydrogen peroxide vapour is not very specific as far as the nature of the catalyst is concerned.

In the first part of this investigation (2) Baker and Ouellet studied the thermal decomposition of hydrogen peroxide vapour on Pyrex in the range 70° to 200° C. with special emphasis on the effect of the shape and size of the reaction vessels. A few trial runs with soda-glass and fused Pyrex vessels indicated that the nature as well as the ultimate treatment of the active surface were important factors in determining the rate of the reaction. Therefore it was felt desirable to extend their work in that direction. An all-glass apparatus was used in order to avoid any contamination of the surface. This also permitted the reaction to be followed at higher temperatures. More than 300 runs were made, the results of which are summarized below.

Experimental

The reaction vessel, in most cases a one-litre round flask *A* (Fig. 1), was placed in a thermostat made either of an oil-bath or, at temperatures above 200° C., of an electric furnace. In both cases the temperature was kept constant to $\pm$ 0.3° C. by means of a mercury regulator or a resistance thermometer and an electronic relay (18). The temperature was measured with a mercury thermometer or a calibrated thermocouple. The reaction vessel could be connected either to the vacuum pump or to the source of hydrogen peroxide, *C*, through a special stopcock of the mercury-seal type, *D*. At first this stopcock was lubricated with only a little graphite to prevent introducing any volatile material into the reaction system. Later on some Apiezon

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M grease was used without any ill-effect. All the tubing containing hydrogen peroxide vapour was heated to 40° C. with a nichrome winding wrapped in asbestos. In order to fill or evacuate the whole system quickly the connecting

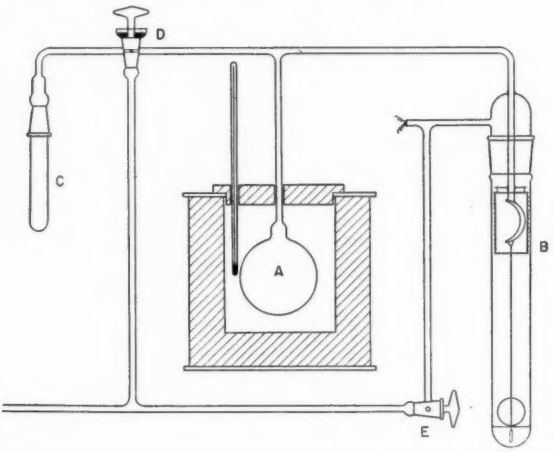

FIG. 1. *Apparatus used in following the decomposition of hydrogen peroxide vapour.*

tubes were made rather large, 8 mm. in diameter. The pressure was measured directly on a Bourdon gauge, *B*, by means of a measuring microscope reading to 0.01 mm. Preliminary calibration against a Dubrovin mercury manometer had shown that the deflection of the gauge was strictly proportional to the pressure differential over a region much wider than that normally used. Two of these gauges were used in succession, the first one (up to Run 264) having a sensitivity of 2.9, and the second one, of 3.7 mm. of mercury per mm. of deflection. To dampen the vibrations the tip of the glass pointer was immersed in Apiezon oil, the vapour pressure of which was so low that it had no appreciable effect on the zero point of the gauge. This was tested frequently and usually was found to remain unchanged over a period of many days. A coiled heater was placed around the upper part of the gauge to prevent condensation of the vapours.

The hydrogen peroxide used was prepared by fractional distillation of a 30% commercial solution. Its concentration was of the order of 95 to 99%; no special care was taken to keep it constant, as the rate of decomposition was known to be independent of the original composition of the vapour (2). It must be mentioned at this point that the vapour contained in the reaction vessel was not in equilibrium, strictly speaking, with the liquid in tube *C* because the two were separated by a length of tubing (in the present case, 60 cm.) that acted as a fractionating column. Since hydrogen peroxide is somewhat less volatile than water this fractionation effect through a narrow tube was not negligible. Therefore the composition of the vapour could not

be calculated accurately from partial pressure data (8). Before starting a run the reaction vessel was evacuated to 0.01 mm. of mercury or better by means of an oil pump. The tube containing the liquid hydrogen peroxide was quickly evacuated and then heated to about 37° C. by immersing in a water-bath. The vapour was then admitted into the reaction system through stopcock *D*. This took usually 10 to 15 sec., after which the rate of the reaction was measured. When enough time had elapsed to take the 'infinity' reading the entire system was evacuated again for another run. In order to avoid introduction of dust particles, air was never admitted into the apparatus during a series of runs. The pressure of the vapour at the beginning of a reaction was of the order of 5 mm. and it never varied much from that value.

Results

Except in a few odd cases mentioned later the results were found to fit the first order equation:

$$k = \frac{2.303}{t} \log \frac{a}{a - x},$$

at least until the reaction was about 90% completed. Towards the end there was a tendency for the reactions, specially the more rapid ones, to slow down somewhat. This effect may be attributed partly to the diffusion into the reaction vessel of the peroxide vapour contained in the connecting tubes, which amounted to 12 to 15% of the total. The reactions in any given series were run as closely as possible to one another and scattered with respect to temperature in order to detect any ageing of the glass surface. The run number is given in each case to indicate the order in which they were carried out. As a rule any given reaction could be duplicated fairly exactly provided the necessary precautions were taken to avoid the slightest alteration of the

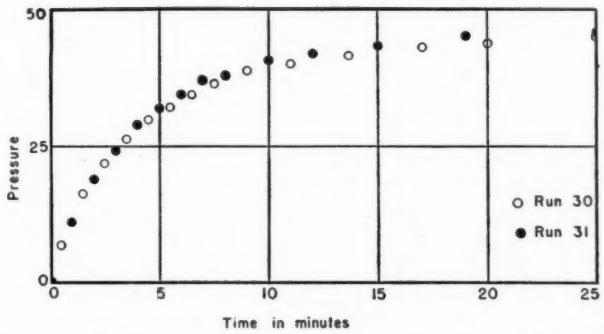

FIG. 2. *Decomposition curves for two consecutive reactions in vessel I at 200.8° C.*

active surface. The curves in Fig. 2 give an idea of the average degree of reproducibility of two consecutive reactions. In all cases the pressures given are readings of the measuring microscope.

I. Decomposition on Pyrex

Reaction Vessel I

The apparatus was first tried out with a Pyrex flask that had been thoroughly cleaned and fused. The regular procedure adopted for the present investigation consisted in cleaning the glass for five minutes with a warm chromic acid solution, rinsing repeatedly with distilled water and finally with redistilled water (conductivity less than 0.1 p.p.m. as sodium chloride). Steaming the flask had the same effect as the final rinsing. Fusing was done by heating, while rotating the flask slowly, in the flame of two Méker burners until the entire surface had been brought in turn to the softening point. This operation took over an hour but very little distortion of the flask ensued. Because of some defect in the apparatus the first 25 runs had to be discarded. Before the necessary alterations could be made, six months had elapsed and, as was found later, the effect of fusing the glass had partially disappeared by then. However, the results obtained under these conditions are reported here (Fig. 3 and Table I) as an example. In order to save space, only the rate constant, obtained graphically, is given for each run. The apparent energy of activation E was obtained from a plot of log k vs $1/T$.

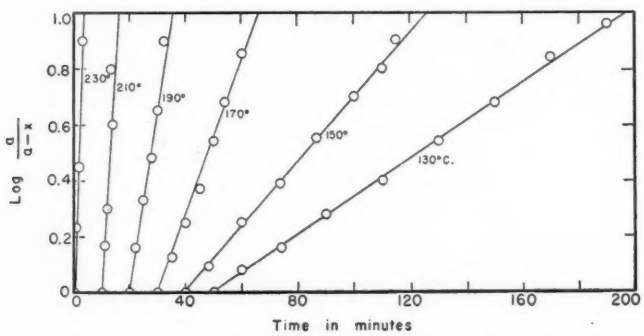

FIG. 3. *Decomposition in reaction vessel I between 130° and 230° C. The curves are shifted along the time axis to avoid confusion.*

Reaction Vessel II

The rates observed with the first vessel were higher than those found by Baker and Ouellet for a fused Pyrex surface. To afford some means of comparison the flask they used (their vessel *H*) was cleaned and fused anew. The activity of the surface was thus very much decreased so that it was possible to follow the reaction up to 375° C. While making these runs the following phenomenon was observed by accident. If the reaction vessel was filled as usual and then most of the hydrogen peroxide vapour pumped out quickly before it had time to decompose appreciably, then on further filling the vessel the reaction seemed to be of zero order until about three-quarters complete (Run 52, Fig. 4). Furthermore the final pressure reading was greater than in a normal run by as much as 50% in some cases, very likely

TABLE I

DECOMPOSITION IN PYREX VESSELS

Run No.	T,° C.	$k \times 10^3$/sec.	Run No.	T,° C.	$k \times 10^3$/sec.
Reaction Vessel I					
37	129.2	0.19	29	181.4	1.65
39	138.6	0.28	31	200.8	3.6
28	159.7	0.78	40	220.5	6.4
35	170.2	1.15	41	231.0	8.6
	E = 15.5 kcal./mole				
Reaction Vessel II					
171	205	0.12	173	300	3.3_5
181	225	0.39	177	325	7.4_3
180	250	0.9_6	174	350	12.3
179	275	2.2_2	175	375	22.2
	E = 18.2 kcal./mole				

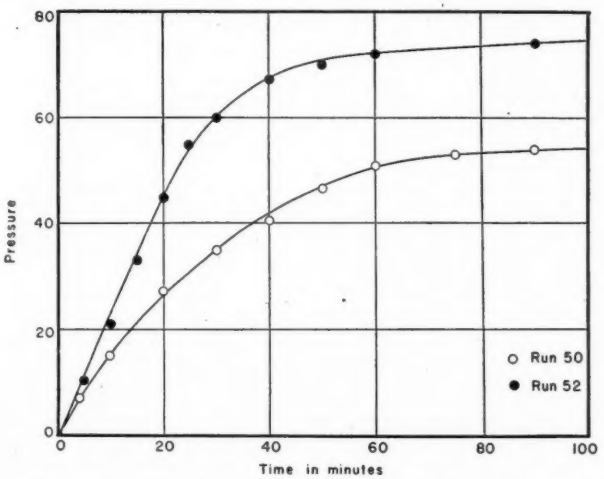

FIG. 4. *Decomposition curves for a Pyrex reaction vessel at 183° C. showing the effect of adsorption due to repeated filling (Run 52).*

owing to a corresponding increase in the amount of hydrogen peroxide present in the reaction vessel. It was possible to duplicate this result fairly closely by repeating the same operations. Similarly the behavior of the reaction vessel reverted to normal upon regular operation. The significance of these observations will be discussed below.

Reaction Vessel III

The above results proved conclusively that two vessels, even if made of the same material, can give widely different rates of decomposition and activation energies. The next series of runs were made to show the effect

TABLE II

DECOMPOSITION IN REACTION VESSEL III

Run No.	T,° C.	$k \times 10^3$/sec.	E, kcal./mole
137	140	1.10	
147	164	3.07	
146	185	5.04	12.6
145	205	9.6	
144	224	15.1	
139	245	25.5	
Fused			
250	240	0.97	18.7
248	260	2.02	
251	289	4.2	
249	305	7.7	
Treated with chromic acid			
257	98	0.48	
255	140	1.45	7.8
253	210	5.7	
Fused again			
261	222	1.77	15.8
260	288	11.6	
Washed with hot water			
265	139	0.52	16.1
262	157	1.08	
266	175	2.54	
Coated with salt (Na_3PO_4)			
270	59	0.77	21.6
272	93	11.8	
269	103	35	
Etched with hydrofluoric acid			
281	130	0.33	
282	148	0.48	8.4
278	162	0.72	
283	225	2.43	

of various treatments on a given reaction vessel. The results observed are summarized in Table II. Fusing a glass (Pyrex) surface reduced its activity by a factor of about 20, while the temperature coefficient of the decomposition increased markedly. This effect was destroyed by cleaning the vessel with hot chromic acid. By repeating these operations the glass surface could be restored to nearly the same activity at least a few times. As could be expected with an heterogeneous reaction, the rate was increased considerably by coating the vessel with a salt. This was done by washing the flask with a saturated solution of trisodium phosphate and draining. Harris (9) has observed a similar phenomenon in the decomposition of hydrogen ethyl peroxide. Etching the glass surface with aqueous hydrofluoric acid also increased its activity, though not as much as was anticipated. After this treatment, however, the reaction became erratic, so that the rates and the temperature coefficient given are not reliable. Extrapolation shows that throughout the above series of treatments it was possible to vary the rate of decomposition by a factor of the order of 10^5.

Reaction Vessel IV

An attempt was made to run the reaction at a temperature as high as feasible in order to detect the possible existence of any homogeneous decomposition of the peroxide vapour. Although no relation between reaction velocity and surface to volume ratio of the vessel has been found (2) because of the difficulty of getting standardized surfaces, it was logical to use a large vessel for this purpose. Out of a number of two-litre flasks taken from the stock available, one was chosen that had a relatively low activity so that the reaction could be followed up to 420° C. (Table III). Yet throughout this interval of more than 260° C. the temperature coefficient of the reaction remained essentially constant.

TABLE III

REACTIONS IN A TWO LITRE PYREX VESSEL (IV)

Run No.	T,° C.	$k \times 10^3$/sec.	Run No.	T,° C.	$k \times 10^3$/sec.
236	156	0.19	240	324	8.5
237	196	0.96	241	372	10.3
238	228	2.43	235	392	12.5
231	257	2.31	242	419	18.0
239	271	5.1	243	419	19.1

$E = 7.5 - 8.0$ kcal./mole

II. DECOMPOSITION ON SOFT GLASS

Reaction Vessels V and VI

It is well known that solutions of hydrogen peroxide decompose more rapidly in soda-glass containers than in Pyrex. This has been generally attributed to the slow solution of the alkaline constituents of the glass that

promote the decomposition of the peroxide. Baker and Ouellet had made a few trial runs with a soft-glass vessel that proved to be very active even at low temperatures. However, the flask they used was old and nothing was known of the composition of the glass itself. The experiments reported here were carried out in soda-lime flasks made specially for this purpose and kindly supplied by the Kimble Glass Co. The first one used was connected to the reaction system through a ground-glass joint held together with a little Apiezon *W* wax. After about 20 normal runs (Nos. 58 to 78) the reactions became erratic and finally were of purely zero order. A second flask connected similarly showed the same phenomenon. Upon investigation it was discovered that a trace of the Apiezon wax had crept inside the glass joint, and, since this wax decomposed hydrogen peroxide violently, it created an active spot. Diffusion of the reagent and products to and from this spot resulted in an apparent zero-order reaction. On replacing the ground joint by a graded seal, the decomposition became normal again. As can be seen from the results in Table IV, the rates of the reaction were markedly different in the two flasks although the flasks were of the same make and subjected to identical treatments. A few runs were tried in vessel V previously evacuated down to 10^{-4} mm. of mercury by means of an oil diffusion pump and a liquid-air trap. As a result the reaction was slowed down to about half its normal value but the temperature coefficient remained unchanged (Table IV). Above

TABLE IV

REACTIONS IN SOFT GLASS VESSELS (KIMBLE'S STANDARD FLINT GLASS)

Run No.	T,° C.	$k \times 10^3$/sec.	Run No.	T,° C.	$k \times 10^3$/sec.
Reaction Vessel V					
58	50.0	0.12_5	After pumping down to 10^{-4} mm. Hg		
59	70.3	0.27_5	61	89.3	0.48
60	89.3	0.72	68	128.5	2.0_2
62	108.6	1.87	76	139.0	2.3_5
69	128.5	3.8	75	159.5	10.4
77	139.0	5.7			
67	147.7	7.7			
74	159.5	18			
E = 11.3 kcal./mole			E = 11.5 kcal./mole		
Reaction Vessel VI					
115	58.8	0.90	100	132.5	14.2
109	80.1	2.03	102	144.9	22.0
111	101.8	5.70	104	154.6	32
95	118.0	8.86	118	154·6	37
			121	154·6	44
E = 10.5 kcal./mole					

150° C. the decomposition became too rapid to be followed accurately; yet there was definite indication that the activity of the vessel increased with time (compare Runs 104, 118, and 121).

The effect of poisons on the catalytic surface was also tested in flask V at 60° C. Some gaseous hydrogen cyanide was introduced at a pressure of 2 mm. and pumped off quickly after a short while. Contrary to what is frequently observed with heterogeneous reactions, no poisoning effect of the catalyst could be detected. This is perhaps not surprising in view of the fact that the heterogeneous decomposition of hydrogen peroxide vapour shows no marked specificity as far as the nature of the catalyst is concerned. Treatment of the glass containers with hydrochloric acid has been advocated to help reduce the decomposition of hydrogen peroxide solutions. This was also tried under the same conditions by admitting gaseous hydrogen chloride into the reaction vessel. After quick evacuation the first hydrogen peroxide vapour introduced decomposed instantaneously, presumably owing to oxidation of the hydrogen chloride. Then, after thoroughly outgassing the system, the reaction slowed down considerably: $t_{½}$ = 180 min. as compared with 8 min. originally. No further tests were made to find out how long this effect lasted.

III. Decomposition on Quartz

The thermal decomposition of hydrogen peroxide vapour on a quartz surface was investigated for the first time by Elder and Rideal (5). They reported a zero-order reaction at 85° C. but the unusual feature was that the decomposition stopped abruptly at about 15% completion; this was interpreted as due to inhibition by oxygen. Later Kistiakowsky and Rosenberg (11) tried to repeat these experiments. They were unable to get reproducible results although they observed no stopping of the reaction short of complete decomposition. Recently Mackenzie and Ritchie (13) have published extensive results on the same subject in the temperature range 15° to 140° C. Again in all cases the decomposition was complete. The present investigation suggests the following explanation for the phenomenon observed by Elder and Rideal. In their apparatus the quartz vessel at 85° to 95° C. was connected, through a fine capillary tubing, to a soft-glass system kept at 120° C. They assumed a very rapid decomposition of the vapour contained in the connecting tubes; yet this may have been what they were actually measuring. To obtain the 'infinity' reading they had to heat the reaction vessel to a much higher temperature, presumably because the decomposition on the quartz was unmeasurably slow or was preceded by an induction period. This would also explain why on freezing out the hydrogen peroxide left in the system and pumping off the oxygen another 15% decomposed. Mackenzie and Ritchie worked at pressures less than 1 mm. with two different cylindrical quartz vessels having volumes of 21.75 and 31.37 ml. and active surfaces of 42 and 54 sq. cm. respectively. In general the reaction was bimolecular with respect to the peroxide pressure. The conditions for the present work were somewhat different.

Reaction Vessel VII and VIII

The first flask used was made of transparent silica (Vitreosil) connected to a graded seal. The results given in Table V show that the reaction was of the first order with about the same rates as on Pyrex. An outstanding feature, however, was the existence of a sort of induction period, during which the

TABLE V

REACTIONS IN QUARTZ VESSELS

Run No.	T, °C.	$k \times 10^3$/sec.*	Induction period, sec.
Reaction Vessel VII (Vitreosil)			
160	105	0.42	750
169	125	1.05	430
158	150	3.2	100
166	175	5.6	20
156	205	12.1	0
163	215	17.2	0
162	220	19.6	
	E = 12.2 kcal./mole		
After fusing			
198	150	1.14	0
194	185	3.9	0
195	250	15.6	0
196	275	33.8	0
	E = 11.6 kcal./mole		
Reaction Vessel VIII (Amersil)			
191	81	3.2	360
193	100	6.7	120
192	152	37.5	0
	E = 10.3 kcal./mole		

* *The rate constants were calculated from the first-order portion of the curves only.*

decomposition was very slow (Fig. 5). The length of this induction period decreased with increasing temperature until it had practically disappeared at about 175° C. However, no exact limit can be assigned there because of the time required for filling the vessel and for allowing the vapour to reach thermal equilibrium. To find out whether or not this peculiarity was specific of quartz, a second flask of the same dimensions but of different make (Amersil) was used. The reaction rates were different but the induction period persisted.

Finally the first flask was fused thoroughly in the blast of an oxygen torch until the quartz became incandescent. This treatment slowed the rate of decomposition to about one-half of its original value and at the same time caused the phenomenon of induction to disappear. The temperature factor of the reaction on quartz in both flasks gave an apparent activation energy of about 12 kcal. per mole.

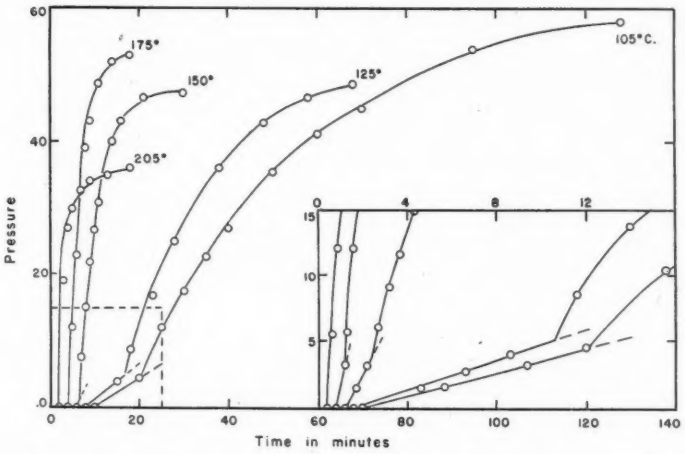

FIG. 5. *Decomposition curves for reaction vessel VII with enlarged section showing the induction periods.*

IV. DECOMPOSITION ON METALS

Most metals, especially when finely divided, are very good catalysts for the decomposition of liquid hydrogen peroxide. There are however a few exceptions such as aluminum, which is relatively inactive so that containers made of it are currently used for storing concentrated solutions of hydrogen peroxide. Pure block tin is also claimed to be quite inert in this respect. It was thought worth while to investigate the effect of these metals on the vapour.

Reaction Vessels IX and X

Because of the difficulty involved in making metal containers of the suitable size and shape, and capable of standing reduced pressure, ordinary one-litre Pyrex flasks were covered inside with pure tin and pure aluminum mirrors deposited by the evaporation method. The coatings were made as thick as feasible by this technique; still, from the point of view of catalysis, such a surface may be quite different from that of a solid metal. The decomposition was followed at only three temperatures in each case but the rates could always be duplicated fairly accurately. As shown by the results (Table VI), the activity of both metals is comparable with that of soft glass and quartz. There is however some uncertainty regarding the values of the activation energy.

TABLE VI

DECOMPOSITION ON METALLIZED SURFACES

Reaction vessel IX (Tin)			Reaction vessel X (Aluminum)		
Run No.	T, °C.	$k \times 10^3$/sec.	Run No.	T, °C.	$k \times 10^3$/sec.
289	72.2	1.12	294	96.5	1.60
287	97.6	3.3	296	129.4	7.7
288	117.3	10.7	298	153.0	12.6
E = 13 kcal./mole			E = 12 kcal./mole		

Discussion

It is obviously impossible at present to account for all the above results. Certainly it would be unwise, in an investigation of this kind, to draw general conclusions from a few particular observations since they may well be fortuitous. For instance, zero-order reactions seem to arise whenever there is a very rapid decomposition on some active centre. Only when data on the diffusion of hydrogen peroxide vapour become available will it be possible to account quantitatively for these phenomena. One particular Pyrex vessel gave reactions with a negative temperature coefficient, possibly owing to a progressive alteration of the surface. In spite of the usual treatments the results remained erratic. Previous workers in this field have encountered a similar situation. Like other fundamental reactions apparently simple, the decomposition of hydrogen peroxide is complex in nature. From the predominance of surface effects and the constant temperature coefficient it would appear that the homogeneous decomposition of the peroxide vapour is still unmeasurably slow at 700° K; this points to a rather large energy of activation. Whatever the mechanism of the reaction there is little doubt that the initial step is through breaking of the O–O bond. Experimental evidence of this has been reported recently (7) in the decomposition of tertiary alkyl peroxides, where the case is much less clear-cut. Now, a number of conflicting values are given in the literature for the dissociation energy of peroxides (not to be confused with the O–O bond energy (16, p. 53)). By a spectroscopic method Geib (6) found 52 kcal. for the dissociation:

$$H_2O_2 = OH + OH \ .$$

Essentially the same result is obtained from the following thermochemical and spectroscopic data:

$H_2O_2 = H_2O + 1/2\ O_2$	$\triangle H = -24$ kcal. (14, 15)
$H_2O = OH + H$	$\triangle H = 118.2$ kcal. (4)
$H + O = OH$	$\triangle H = -100.1$ kcal. (4)
$1/2\ O_2 = O$	$\triangle H = 59.1$ kcal.
$H_2O_2 = 2OH$	$\triangle H = 53.0$ kcal.

Lewis and von Elbe (12, p. 385) reported a substantially lower value, 43 kcal., while Ubbelohde (19) used 48 kcal., but in neither case was it mentioned on what evidence. Values ranging from 51 to 66 kcal. (3, 20) have been found for the dissociation of various organic peroxides although it can be argued that in these compounds the O–O bond is stabilized by transfer of negative charges to the oxygen atoms. Therefore 52 kcal. seems a plausible figure for the dissociation of hydrogen peroxide. Assuming that the homogeneous decomposition proceeds unimolecularly, this would represent a lower limit for the energy of activation. However, it has not yet been possible to determine the nature of the gas reaction because of the overwhelming importance of the catalysis at all temperatures and on any surface. Semenoff (17, p. 419) believed that it would be a chain reaction on account of its resemblance with the photochemical decomposition (1), which has been shown to take place through very long chains (of the order of 10^4 to 10^7 units) in solution at least. Previous investigations (2, 13) have indicated, on the contrary, that long chains play no great role in the case of the vapour. Still it is possible that the conditions were not favourable then to the formation or the propagation of chains.

The catalytic decomposition of hydrogen peroxide is peculiar in that there is no very specific action of the active surface. To be sure, the observed rates vary appreciably from one catalyst to another as shown above but, on the whole, results of the same order of magnitude were found with such widely different surfaces as glass, metals, and paraffin oil. It seems like a case of physical rather than chemical adsorption. The polar character of the hydroxyl group leads to adsorption on any surface. The hydrogen peroxide molecule is thus oriented and the relatively weak O–O bond is strained so that only a low thermal activation is required for the dissociation. All surfaces will therefore decompose the peroxide vapour at an appreciable rate at moderate temperatures. Even so, the values observed for the apparent energy of activation, 8 kcal. and even as low as 4 in some instances (13), seem very small indeed in view of what has been said above. This is a fairly sure indication that the mechanism of the normal reaction is modified by the catalyst. Experimental data are lacking on the adsorption of hydrogen peroxide vapour, but off-hand one would expect its temperature coefficient to be about the same as for water, on the basis of the polarity of the two molecules.

Inspection of the curves in Figs. 6 and 7 reveals the absence of correlation between the apparent energy of activation and the reaction velocity. For quartz, soft glass, and the two metals investigated, the slopes are generally the same as for untreated Pyrex, whereas the rate constant changes by a factor of 15 between the two extreme cases. Very likely this is caused by variation in the number of adsorbed molecules, related to factor A in the modified Arrhenius equation:

$$k = A\, e^{-(E-\lambda)/RT},$$

where E is the true energy of activation and λ, the energy of adsorption of the reactant. The slowing-down effect caused by fusing is no doubt due to a

smoothing of the surface. As already mentioned, freshly fused glass shows a marked tendency to become more active on ageing until it reaches a sort of equilibrium state. This behaviour is possibly the result of incipient crystallization in a supercooled medium. On the other hand, the activation caused by acid washing has generally been attributed to a selective solution of the

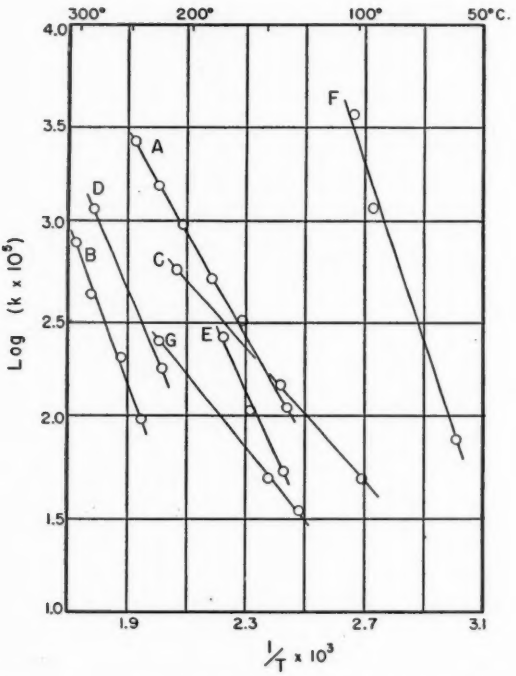

FIG. 6. *Temperature coefficient of the reactions in Pyrex vessel III variously treated. A = normal; B = fused; C = treated for five minutes with hot chromic acid; D = fused again; E = washed with hot water; F = coated with salt; G = etched with hydrofluoric acid.*

more soluble components of the glass, which leaves a sponge-like structure. This view is substantiated by the observation that a simple washing of the fused surface with hot water (Vessel III) increased its activity considerably. The present investigation was completed when the attention of the author was drawn to the fact that the common practice of cleaning glassware with chromic acid has been shown to leave a film of chromium oxides which are not removed even by numerous washings (Prof. F. G. Keyes, M.I.T.; private communication). Consequently the reaction rates reported above must be too high. It is not believed, however, that the general trend of the results was appreciably affected. At any rate curves *C* and *G* (Fig. 6) seem to be definitely in a class by themselves.

The large increase in the amount of hydrogen peroxide present in the reaction system proves beyond doubt that adsorption is responsible for the zero-order reactions on a Pyrex surface (Run 52) as well as for the induction periods on quartz. Complete saturation of all the active centres may have occurred in the former case. Zero-order decompositions were found by Elder

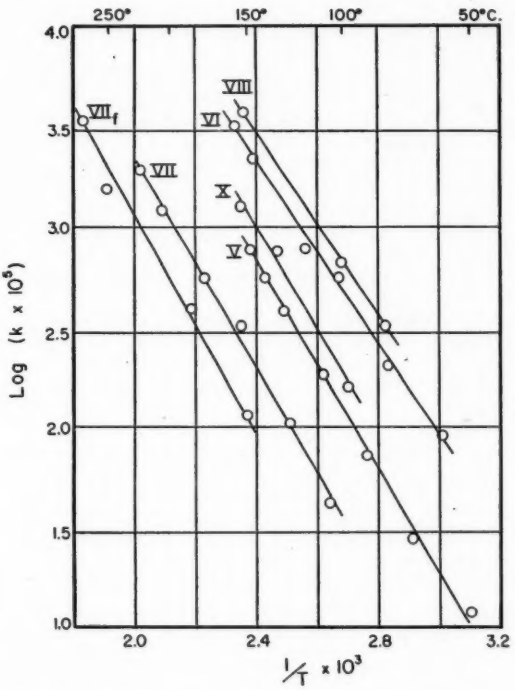

FIG. 7. *Temperature coefficient of the decomposition on soft glass, quartz, and aluminum surfaces. The numerals refer to the reaction vessels.*

and Rideal (5) for the peroxide vapour on glass and by Williams (21) for the liquid on a quartz surface. Short induction periods have also been observed in the thermal decomposition of diethyl peroxide (10). No attempt has been made here to calculate the absolute reaction rates. The mere fact that two similar vessels (V and VI) made from the same batch of glass and treated exactly alike had rates differing by a factor of four, and apparent heats of activation differing by 10%, shows what little significance such calculations would have.

Acknowledgment

The author wishes to express his indebtedness to Dr. Cyrias Ouellet for his continued interest in this work and for many helpful discussions.

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

LXII. EFFECT OF HOT ALKALI ON THE NITRATES OF STARCH, AMYLOSE, AND AMYLOPECTIN[1]

By W. R. Ashford[2] and Harold Hibbert[3]

Abstract

The nitrates of starch, amylose, and amylopectin were treated with hot aqueous sodium hydroxide solution and the effect of this treatment upon each noted. This treatment does not cause appreciable denitration, nor does it result in a usefully stable nitrate. The nitrates of the starches are more resistant to alkali than is cellulose nitrate. Amylose nitrate appears to resemble cellulose nitrate in being more alkali-labile than either whole starch nitrate or amylopectin nitrate; this is consistent with its linear chain structure. The greater stability of amylose nitrate as compared to amylopectin nitrate is paralleled by a greater alkali-lability of the former, which indicates that the inherent instability of starch nitrate is not due to the presence of free terminal aldehyde groups present either in native starch or formed during the nitration process.

Introduction

If starch is treated with hot dilute sodium hydroxide solution, there is formation of simple organic acids and reducing substances. Assuming a potential free aldehyde group at the terminus of the starch molecular chain, then these reducing substances could be produced in a manner analogous to their production in the reaction between aqueous alkali and an aldose sugar (2). Taylor *et al.* (6) and Schoch and Jensen (4) have defined this sensitivity of starch to alkali as 'alkali-lability' and according to the latter authors this lability is expressed as 'alkali-number', which represents the number of millilitres of 0.1 *N* sodium hydroxide consumed by 1 gm. of starch when heated in this solution for one hour at 100° C. Alkali-lability serves only to indicate whether the aldehyde content of the starch has remained constant or whether it has increased or decreased. This in turn serves to indicate hydrolytic changes (3). Starches that have not been subjected to hydrolysis have a negligible or low alkali-lability (6). Schoch believes that the alkali consumption results from the sole interaction of the alkali with free terminal aldehyde groups, and he has shown (5) that the α-1,4- and the β-1,4-glucosidic linkages in maltose and cellobiose respectively are stable to alkali.

During the work described by the authors (1) on the fractionation and nitration of starch it became of interest to observe the effect of hot aqueous

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sodium hydroxide upon amylose and amylopectin (separated by the adsorption of the amylose upon cotton cellulose) and upon the nitrates of these substances as well as whole starch nitrate. No attempt was made to duplicate Schoch's 'alkali-lability' method, a stronger alkali solution and a shorter time of reaction being employed. However, the same fundamental reaction should take place as that described by the latter author.

By a casual observation of the reaction between alkali and starch nitrate, one would expect two possible reactions, the first, a denitration and the second, subsequent to or coincident with the first, a reaction similar to that which Taylor and Schoch have described for starch. Experiments showed, however, that under the conditions used, namely, treatment of the nitrate for 15 min. with hot sodium hydroxide solution (0.3928 *N*), there is no denitration in the case of starch nitrate, amylose nitrate, or amylopectin nitrate. This is quite possible, if, as has been suggested for starch, the alkali attacks only the terminal aldehyde grouping of the starch nitrate molecular chain, leaving the remainder of the chain unaffected. The starch molecule having undergone considerable hydrolysis during the nitration reaction would normally contain an increased number of these terminal aldehyde groups. In the case of whole starch nitrate (Table I) the nitrogen content was slightly greater after alkali treatment than before, while with amylose and amylopectin nitrates the reverse was true. With whole starch at least, it would appear then that the nitrate groups on the nitrated starch chain are stable to alkali. With whole starch nitrate, 70% of the material was dissolved by treatment with aqueous alkali (0.3928 *N*) for 15 min. at reflux temperature. The undissolved residue was a pure white powder when dried, while the solution containing the dissolved nitrate was deep reddish-brown. The residual undissolved material was tested for its stability by means of the Bergmann–Junk test and a value of 10.53 mgm. of nitrogen evolved per gram of nitrate was obtained, indicating very poor explosive properties.

The amylose and amylopectin used in these experiments were obtained by the method previously described (1) whereby the amylose is separated from the amylopectin by adsorbing the former on cotton cellulose, from which it is easily removed by means of boiling water. As shown in Table I, a 250 mgm. sample of amylose was completely solubilized by sodium hydroxide (0.3928 *N*) in 15 min. In the case of amylopectin, complete dissolution did not take place and in neither case was there any appreciable consumption of alkali. When the nitrates of these two substances were treated with alkali there was considerable consumption of alkali, the amylose nitrate using 3.65 milliequivalents and the amylopectin nitrate 2.79 milliequivalents. This would indicate considerable hydrolysis during the nitration. Presumably this involved liberation of additional terminal free aldehyde groups (4, 6) to an equal extent in both cases since the basic chain structure of amylose and amylopectin is considered to be the same (α-1,4-glucosidic linkages). Therefore the nitration of amylose resulted in the formation of more terminal aldehyde groupings than in the case of the nitration of amylopectin.

TABLE I

EFFECT OF HOT ALKALI UPON THE NITRATES OF STARCH, AMYLOSE, AND AMYLOPECTIN

Substance treated	Treatment	Result	Recovered Product
Starch nitrate % N, 12.83	Refluxed for 30 min. with NaOH (0.3928 *N*)	70% nitrate dissolved	% N, 13.32 Abel heat test—25 min. *Bergmann–Junk test—10.53 mgm. N_2 Ash, 0.31%
Starch nitrate % N, 12.83	Refluxed for 30 min. with NaOH (0.1227 *N*)	20% nitrate dissolved	*Bergmann–Junk test—8.12 mgm. N_2
Cellulose nitrate % N, 12.5	Refluxed for 30 min. with NaOH (0.3928 *N*)	Complete digestion to dark red solution	
Amylose	250 mgm. sample refluxed in 25 cc. NaOH (0.3928 *N*) for 15 min.	Complete dissolution. Alkali consumed—negligible	
Amylopectin	As for amylose	Flocculent globules remained undissolved. Alkali consumed—negligible	
Amylose nitrate % N, 13.15	0.5 gm. refluxed in 25 cc. alkali (0.3928 *N*) for 15 min.	Incomplete solution. Alkali consumed—3.65 milliequivalents	% N, 12.95
Amylopectin nitrate % N, 13.25	As for amylose nitrate	Incomplete solution. Alkali consumed—2.77 milliequivalents	% N, 13.02

* *Mgm. of N_2 evolved per 1.0 gm. sample of nitrate.*

In a previous paper (1) it was shown that amylose nitrate is more stable than amylopectin nitrate by means of the Bergmann–Junk test. From the results of the alkali treatment of these two substances it would seem that the higher alkali consumption of amylose nitrate is associated with a greater stability of this substance as compared with a lower alkali-lability of the less stable amylopectin nitrate. The instability of these polysaccharide nitrates cannot, then, be associated with the presence of free aldehyde groups, a conclusion borne out by the fact that the more stable cellulose nitrate is as readily attacked by alkali as is amylose nitrate and considerably more readily attacked by this reagent than is amylopectin nitrate. The agreement in the ease with which amylose nitrate and cellulose nitrate are attacked by alkali points to a similarity in their structure.

Experimental

A suspension of the nitrate (0.5 gm.) in standard sodium hydroxide solution (25 cc.) was refluxed for 15 min. with intermittent shaking of the flask. Cold distilled water (50 cc.) was then added through the condenser and the solution titrated at 15° C. with standard nitric acid using phenolphthalein as indicator.

In cases where larger amounts of nitrate were used, the undigested portion, after the alkali treatment, was removed by filtration. The alkali was then removed from this material by boiling under reflux with distilled water, for periods of 50 hr.

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

LXIII. THE STABILITY OF MALTOSE AND CELLOBIOSE OCTANITRATES[1]

By W. R. Ashford,[2] T. H. Evans,[3] and Harold Hibbert[4]

Abstract

Cellobiose and maltose were nitrated and their properties studied to note the effect of the difference in glycosidic linkage (β- and α-respectively). Cellobiose octanitrate is more stable than maltose octanitrate as measured by the Abel test, and both are less stable than cellulose and starch nitrates. Neither of the octanitrates is sufficiently stable to permit of the application of the Bergmann–Junk test. If the stability of the cellulose nitrate building unit, namely, cellobiose octanitrate, carries over into its polymeric form, it would be expected that cellulose nitrate (characterized by 1,4-β-glucosidic linkages) should be inherently more stable than starch nitrate (α-1,4-glucosidic linkages).

Discussion

The nitrates of maltose and cellobiose were prepared and studied for the purpose of comparing the properties, particularly stabilities, of the fundamental building units of starch and cellulose respectively. Cellobiose octanitrate has not been characterized previously.

The two major chemical differences between starch and cellulose are (*a*) the type of glycosidic linkage (α- and β- respectively) and (*b*) the presence of branched chains in the former (5, pp. 143-182). It seemed that any difference due to glycosidic linkages (α- or β-) might be made apparent from a study of these disaccharides, and that these would provide a possible explanation of the relative instability of starch nitrate.

The nitrates of maltose and cellobiose were prepared as white amorphous solids in high yields by the nitration method described previously (1). Like the corresponding polysaccharides they were insoluble in water and were precipitated from their solution in concentrated nitric acid by the addition of concentrated sulphuric acid.

The fact that cellobiose nitrate was obtained in higher yields (191%) than maltose octanitrate (183%) indicated that during nitration hydrolysis took place to a somewhat greater extent in the case of the latter, a result to be expected in view of the presence of the α-linkage in maltose (4).

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Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, Montreal, Que. Taken from a thesis submitted to the Faculty of Graduate Studies and Research by W. R. Ashford in May 1943 in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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The products were purified by an initial treatment with charcoal and anhydrous sodium sulphate in methanol solution. The maltose derivative was then recrystallized from diethyl ether and the cellobiose derivative from ethanol. The crude nitrates were much more soluble in methanol, ethanol, diethyl ether, etc., than when more highly purified, this being especially true of cellobiose octanitrate. Both substances showed a marked tendency to separate from solution in the amorphous state, but crystallization could be induced by very slow concentration of these solutions at room temperature. The crystalline structure of both compounds appeared to be the same, namely, needles arranged in the form of tiny rosettes.

The melting point of the crude products was very indefinite (70° to 90° C.) owing to the presence of glucose pentanitrate (m.p. 10° C.). The purified maltose octanitrate melted at 163° to 164° C. and the cellobiose octanitrate at 154° to 155° C.

Properties of the Nitrates

Their analyses (Table I) corresponded to those of the pure octanitrates.

TABLE I

PROPERTIES OF MALTOSE AND CELLOBIOSE OCTANITRATES

Property	Maltose octanitrate	Cellobiose octanitrate
Nitrogen content, %	15.87 (theoretical—15.95)	15.91
Molecular wt. (Rast method)	699 (Calculated—702)	698
Abel test, min.	18	32
Bergmann–Junk	Both products too unstable to stand the test	
Alkali-lability*	7.97	13.82

* *Milliequivalents of sodium hydroxide (0.0567 N) consumed during 30 min. refluxing.*

The Abel test indicated that the cellobiose nitrate was the more stable, while neither compound was of sufficient stability to withstand the Bergmann–Junk test for the usual period (two hours).

On alkali treatment (2), cellobiose octanitrate consumed more alkali than did the maltose compound; 13.82 and 7.97 milliequivalents of sodium hydroxide (0.0567 *N*) respectively. This result is to be compared with those of previous experiments (2) where cellulose nitrate consumed more alkali than starch nitrate.

On the basis of these results it was concluded that cellobiose octanitrate possesses slightly greater stability than maltose octanitrate and that, if this difference is cumulative, then cellulose nitrate should be inherently more stable than starch nitrate.

Experimental

Preparation of Cellobiose

The cellobiose was prepared from cellobiose octaäcetate by hydrolysis with sodium methylate in absolute methanol (3).

Nitration

Cellobiose (13 gm.) was nitrated, according to the procedure used for whole starch (1, 6), with nitric acid (95 cc., sp. gr. 1.5) and sulphuric acid (110 cc., 96.5%). The cellobiose dissolved immediately in the nitric acid and the nitration was allowed to proceed for one hour. Concentrated sulphuric acid precipitated the nitrate as a gummy mass, which was ground in a mortar with ice-water to yield a pulverulent mass. The product was filtered and washed until acid-free by refluxing in distilled water for at least 25 hr.

Maltose (Kahlbaum) was nitrated in a manner identical with that used for cellobiose.

Both nitrates were white amorphous solids, insoluble in water. The crude products were unstable, especially the maltose preparation, which decomposed slowly at 50° to 55° C.

The yields of crude products were: maltose nitrate, 183.2; cellobiose nitrate, 191.0% (theoretical, 205.3%).

Purification

(*a*) *Maltose octanitrate.*—A methanolic solution of crude maltose octanitrate was treated with charcoal at 40° to 50° C., then dried with anhydrous sodium sulphate. The removal of methanol under reduced pressure at room temperature caused the nitrate to separate in crystalline form (needles in rosette formation) (m.p. 95° C.). The crude crystals were dissolved in diethyl ether, from which glucose pentanitrate and maltose octanitrate were separated by fractional crystallization. The ether solution of the crude crystalline product was allowed to stand at room temperature, and, on evaporation of the solvent, deposited a good yield of crystalline maltose octanitrate, leaving the glucose pentanitrate in solution. Recrystallization from ether did not change the melting point (163° to 164° C.) Reported value, 163° to 164° C. (6).

(*b*) *Cellobiose octanitrate.*—The crude product was treated with methanol, charcoal, and anhydrous sodium sulphate as was the maltose octanitrate. The first crop of crude crystals had an indefinite melting point of 85° to 95° C. These crystals were recrystallized from ethanol and gave a product melting at 149° to 150° C. Recrystallization from ether–methanol solution (2 : 1) raised the melting point to 154° – 155° C., which did not change on subsequent recrystallizations.

Properties of the Nitrates

The nitrates were examined for their nitrogen contents, molecular weight, stability, and their alkali-lability, with the results shown in Table I. Methods for nitrogen content and stability were those described previously (1). Molecular weights were determined by the method of Rast.

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TERTIARY MERCAPTANS AS MODIFIERS IN GR-S POLYMERIZATIONS[1]

By Maurice Morton[2] and R. V. V. Nicholls[3]

Abstract

Tertiary octyl, decyl, dodecyl, and hexadecyl mercaptans were investigated as modifiers in GR-S polymerizations.

The rate of disappearance of these modifiers followed a first-order rate equation during the first half of the polymerization, in accordance with the theory of chain-transfer reactions. During the latter part of the reaction, an increased rate of disappearance generally occurred. A mechanism is suggested.

The rate of disappearance increased with decreasing chain-length of the mercaptan. The intrinsic viscosities and molecular weight distributions of the polymers obtained at different conversions were related to the activity of each mercaptan as a modifier. Values for the regulating index of each mercaptan were calculated.

The slow rate of disappearance of tertiary hexadecyl mercaptan leads to the formation of polymer that is relatively homogeneous in molecular weight, and this mercaptan is therefore a desirable modifier. However, after 50% polymerization, the regulator action shows a marked acceleration, leading to the formation of progressively lower molecular weight polymer and resulting in a spread in the molecular weight distribution.

Introduction

The regulation of molecular size during polymerization by compounds, such as mercaptans, is usually termed 'modifier action'. The mechanism of such modifier action has been the subject of intensive study, especially in connection with the GR-S polymerization. A great deal of evidence has been presented in support of the view that modifiers, such as the mercaptans, act as chain-transfer agents (11, 13). This mechanism presupposes that the growing polymer chain is terminated by a hydrogen atom from a mercaptan molecule, the remaining mercaptan free radical acting as an initiator of a new polymer chain.

On the basis of such a chain-transfer mechanism, Ewart, Smith, and Hulse (4) developed a kinetic relation for the rate of disappearance of mercaptan during polymerization. From this kinetic relation they also derived the manner in which the molecular weight of the polymer formed should vary during the course of the polymerization. Their experimental data on the emulsion polymerization of butadiene showed good agreement with theory at low conversions.

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By means of a simple mathematical treatment of the polymerization reaction, Ewart *et al.* derived a function that they termed the 'regulating index' of a modifier. This function is defined as follows:

$$r = -\frac{d \ln R}{dP} , \tag{1}$$

where P = number of grams of polymer formed per gram of initial monomer, at any time.

R = concentration of regulator, expressed as moles of regulator per gram of initial monomer,

r = a constant known as the 'regulating index',

The value of r thus represents the activity of any modifier in its action as a chain-transfer agent. From this a relation was derived between the regulating index of a modifier, its concentration at any time, and the polymer chain-length being formed at that time, thus:

$$M_R = \frac{1}{rR} , \tag{2}$$

where M_R = number-average molecular weight of polymer produced at that particular instant.

Ewart *et al.* termed M_R the 'regulator theory molecular weight', but it is evident that it is in fact identical with the number-average molecular weight, in the absence of chain branching.

It is important to note that the derivation of this regulating index of modifiers is based upon one basic assumption made by Ewart *et al.*, and expressed thus:

$$-\frac{dR}{dP} = rR . \tag{3}$$

Such an assumption could be valid under conditions where the rate of polymerization is independent of monomer concentration. This condition is actually found to be true, at least up to conversions of 70%, in the case of the GR-S emulsion polymerization, although it is contrary to the classical rate equation derived for bulk polymerization systems. The classical expression for the propagation step in polymerization is represented by

$$\frac{dP}{dt} = k_1 [A^{\cdot}] [M] ,$$

where $[A^{\cdot}]$ = concentration of active centres,

$[M]$ = concentration of monomer.

For the GR-S system, assuming monomer concentration remains constant, this becomes

$$\frac{dP}{dt} = k_2 [A^{\cdot}] . \tag{4}$$

The rate equation for modifier consumption, based on a chain-transter mechanism, is represented by

$$-\frac{dR}{dt} = k_3 [A^{\cdot}] R . \tag{5}$$

It can be seen that by dividing Equation (5) by Equation (4) there is obtained an expression identical with Equation (3).

It must be emphasized that the above deductions are applicable only to a case such as the GR-S polymerization, where the emulsion system apparently prevents the depletion of monomer from affecting the rate of polymerization until high conversions are reached.

Tertiary aliphatic mercaptans have been known for some time to possess the ability of regulating the molecular size of polymers and of acting as promoters in GR-S polymerization. The term 'promoter' refers to the well known fact that mercaptans have the ability of enhancing the effect of a catalyst such as potassium persulphate, and thus increasing markedly the rate of polymerization. Hence it was considered of interest to investigate more fully the action of various tertiary mercaptans as modifiers, in an attempt to establish a regulating index for each and to correlate molecular size of the polymer with each regulating index. The data presented in this paper have been obtained for the purpose of determining as carefully as possible exactly how the character of the polymer changes in the course of polymerizations carried out with various tertiary mercaptans. The studies to date have been carried out only on Sharples' tertiary octyl, decyl, dodecyl, and hexadecyl mercaptans.

Experimental Procedures

The following methods of investigation were used in the evaluation of this series of tertiary mercaptans:

1. GR-S polymerization using various tertiary mercaptans at several different initial concentrations;
2. Determination of rate of polymerization;
3. Determination of rate of mercaptan disappearance;
4. Characterization of the polymer,
   (*a*) Coagulation and drying of the polymer,
   (*b*) Sol–gel separation,
   (*c*) Determination of the intrinsic viscosity of the polymers obtained at different conversions,
   (*d*) Determination of a precipitation-distribution function for the polymers obtained at different conversions.

The experimental technique and materials used are described below.

1. Polymerization

Apparatus

The polymerizations were carried out in the standard 4-oz. round-form bottles, with metal screw caps. The caps were fitted with Neoprene liners, which were always extracted with hot acetone before use. The bottles were rotated end over end in a water-bath maintained at 50° ± 1° C., and fitted

with a horizontal shaft to which were attached the bottle clamps at a radius of about 8 in. The speed of rotation was about 30 r.p.m.

It might be stated at this point that several attempts were made, at the beginning of this investigation, to use the tube polymerization method as outlined by Fryling (6). It was found, however, that erratic results were obtained with this technique, some kind of inhibiting action being noticeable and leading to low, non-reproducible conversion rates. Strangely enough, although this erratic effect occurred with the use of tertiary mercaptans, it was not noticeable when OEI (technical *n*-dodecyl mercaptan) was used as a modifier. No explanation has been offered for this behaviour.

Materials

The Mutual Recipe was used, with variations only in the kind and amount of mercaptan used, as follows:

POLYMERIZATION RECIPE (PARTS BY WEIGHT)

Water	180
Soap	6
Potassium persulphate	0.3
Mercaptan	Variable
Styrene	25
Butadiene	75

The soap used was the household variety of Ivory Flakes, stored in the dark in a tightly stoppered container in order to avoid peroxide formation. Periodic control runs were carried out to check the uniformity of the soap flakes.

Potassium persulphate used was Merck's Analytical Reagent grade.

Styrene* used was received from the Dow Chemical Company of Canada, Sarnia, Ont. This styrene was inhibited with 10 p.p.m. of *p*-tertiary butyl catechol. After several control runs it was found that identical results were obtained whether the styrene was redistilled, or used as received. Hence, in all runs, the styrene was used as received, i.e., with the inhibitor present.

The butadiene* used was received from the Canadian Synthetic Rubber Limited, Sarnia, Ont. It was purified by bubbling through a 2 *N* solution of sodium hydroxide to remove any inhibitor (300 p.p.m. of *p*-tertiary butyl catechol), and then through a glass U-tube, packed with glass wool and kept at $-5°$ C. The purified butadiene was collected in a dry ice – acetone trap, from which it was apportioned to the required charges.

The tertiary mercaptans* were obtained from the Sharples Chemicals Inc., Philadelphia, Pa. The following mercaptans were used:

Tertiary octyl mercaptan (Sharples 2-B)
Tertiary decyl mercaptan
Tertiary dodecyl mercaptan (Sharples 3-B)
Tertiary hexadecyl mercaptan (Sharples 4-B)

* *We desire to acknowledge donations of generous samples of these materials.*

The amounts of these mercaptans obtainable at the time were too small for a purification by fractionation, except in the case of the 3-B mercaptan, of which a plentiful supply was available. Hence the 3-B mercaptan was fractionally distilled under reduced pressure, and the main fraction, which had a constant refractive index, was collected for use. The physical constants of the main fraction obtained from the 3-B mercaptan are shown below, together with the mercaptan content, as determined by amperometric titration with silver nitrate, according to the method of Kolthoff (8).

This main fraction constituted over 90% of the mercaptan as received.

Physical constants of main fraction from Sharples 3-B mercaptan: specific gravity (d_4^{20}), 0.867; boiling point (16 mm.), 112° C.; refractive index (N_{25}^D), 1.4655; mercaptan content (as $C_{12}H_{25}SH$), 98.1%.

The mercaptan content of the other three mercaptans was also determined, and was found to be as follows: octyl, 95.6; decyl, 97.0; hexadecyl, 97.6%.

Procedure

A total charge of 98.0 gm. was used for all bottles, leaving a free space of 10 to 15 cc. The aqueous solution containing the soap and potassium persulphate was added first, then the styrene, containing the required mercaptan. The bottle was then chilled in ice-water, and a slight excess of liquid butadiene added. The cap was then loosely placed on the bottle, and the excess butadiene allowed to evaporate until the bottle assumed the desired weight. It was then capped tightly, a rubber glove being used to apply the required torsion on the screw cap to prevent leakage. All bottles were tested to 200 lb. per sq. in. pressure before use. Any leakage could usually be detected when the bottles were first placed in the water-bath, but, in addition, each bottle was reweighed at the conclusion of the run.

2. Determination of Rate of Polymerization

Procedure

At periodic intervals (usually after 2, 4, 6, 9, and 12 hr.) duplicate bottles were removed from the water-bath and chilled in ice-water at 0° C. Each bottle was then opened and 0.1% hydroquinone added, based on initial monomer weight, as an inhibitor of any further polymerization. The latex was then sampled by the 'stopcock method' as described by Medalia (10), care being taken to shake the latex vigorously before sampling. The size of the sample was usually about 10 gm., which could be weighed on a torsion balance with an accuracy of ± 0.02 gm. It was found necessary to use a 'venting factor' owing to loss of butadiene during sampling, especially for low-conversion polymers. This factor was determined as follows.

The loss in weight of the bottle containing the latex was taken as the true weight of the latex removed. The sample of latex, which was usually in a small beaker, was then warmed gently (30° to 40° C.) and shaken until it showed no further loss in weight. The final weight of this latex sample was then considered as the 'vented weight'. All subsequent work on the vented

latex was always corrected by the use of the proper factor in order to calculate all results on the basis of the original latex in the bottle. The sample of latex thus obtained was used both for the determination of the per cent conversion and for the analysis of the amount of remaining mercaptan.

The conversion was determined by the total solids method. A 1 gm. sample of the vented latex was dried to constant weight at 105° C. in one or two hours. Duplicate determinations were usually carried out on the contents of each bottle. Agreement between duplicate determinations was of the order of ± 2 parts per thousand for high conversion latex and somewhat worse for low conversion latex, apparently owing to difficulty in uniform sampling due to the instability of the emulsion at low conversions. Agreement between duplicate bottles was of the order of ± 5 parts per thousand or better for high-conversion latex and somewhat worse for low conversion latex.

3. Determination of Residual Mercaptan

A portion of the same sample obtained for the determination of the conversion was used for mercaptan analysis. The method used was the amperometric titration with silver nitrate, using a rotating platinum electrode, as described by Kolthoff and Harris (8). The latex was coagulated by dropwise addition to 100 ml. of rapidly stirred absolute ethanol. In order to complete the coagulation and to reduce the residual persulphate, there was added 1 ml. of a solution that was 1 *N* with respect to sulphuric acid and 0.1 *N* in ferrous ammonium sulphate. Size of the latex sample was usually 5 gm., and the strength of the silver nitrate solution was either 0.005 *N* or 0.002 *N*, depending on the amount of mercaptan to be determined. Since the titrations were carried out in the presence of coagulated polymer, care was taken to have a fine, curdy precipitate, with no lumps that might trap some of the mercaptan. Duplicate determinations on the same sample of latex were found to agree within ± 5 parts per thousand, while duplicate bottles gave results that agreed within ± 10 parts per thousand.

4. Characterization of Polymer

(a) Coagulation and Drying

Before proceeding with the characterization of the polymer, it was necessary to coagulate the latex and to thoroughly dry the resulting polymer. The coagulation was carried out by pouring the latex slowly into rapidly agitated *n*-butanol, and the resulting curd was washed well with distilled water to remove all traces of soap. The wet polymer was then dried *in vacuo* at 40° C. It was found that, at 5 mm. pressure, between 48 and 72 hr. of drying was sufficient for polymer samples under 10 gm. in weight. Owing to the coagulation in alcohol, it was not possible to incorporate any antioxidant into the polymer, since the antioxidant would dissolve readily in the alcohol. Hence the polymer obtained was never allowed to stand longer than two weeks, even in the dark, as it was feared that some deterioration might result. It was

actually found that polymer that had originally been completely soluble in benzene developed a considerable proportion of insoluble gel on standing for two months at room temperature in the dark.

(*b*) *Sol – Gel Separation*

Solutions of the polymers were usually made up by placing finely shredded polymer in reagent grade benzene and allowing to stand for at last 48 hr. in the dark. In the case of polymer of low molecular weight ('sticky polymer'), the solution was made up with 2.1 gm. of polymer in 350 cc. of benzene. For polymer of higher molecular weight, the solution consisted of 1.4 gm. polymer in 350 cc. of benzene. This procedure usually yielded solutions having the proper concentration both for intrinsic viscosity determinations and for precipitation studies. The solutions, contained in stoppered flasks, were gently swirled on the second day, in order to promote mixing. After 48 hr., the solutions were examined for any visible gel, and then very carefully decanted through a layer of glass wool supported on a 100 mesh stainless steel wire screen. The amount of insoluble material was then determined indirectly from the concentration of the filtered solution. This was done by evaporating 25 cc. of this solution to dryness in an oven at 70° C.

The above method usually gave a good separation of sol from gel, since it was found that the resulting solution could pass easily through a coarse Pyrex frit. This test, according to Baker and Mullen (2) is very sensitive to dispersed gel, since as little as 0.5 mgm. of highly swollen gel will clog the frit completely. In one or two cases it was found that the gel was apparently so fragile that some of it passed through the glass wool and into the solution, preventing the latter from being passed through the Pyrex frit. In these cases it was sometimes found desirable to carry out a sol–gel separation in a Baker Cell (2) where the gel received more gentle treatment. Obviously, in this type of investigation, the accurate determination of gel content is not of great consequence, since the real interest lies in polymers that are completely soluble and capable of characterization as to molecular size.

(*c*) *Determination of Intrinsic Viscosity*

The viscosities of the polymer solutions were determined by means of an Ostwald type viscometer. The viscometer used had an outflow time of about 130 sec. for pure benzene, so that the kinetic energy correction was very small. This correction was determined by calibrating the viscometer by means of three different liquids, viz., benzene, *n*-heptane, and carbon tetrachloride, and applying the standard viscosity equation (1, 3), which has the form

$$\gamma = Ct - \frac{B}{t},$$

where γ is the kinematic absolute viscosity,
C is the instrument constant,
B is the kinetic energy constant,
t is the outflow time.

Hence by using any two liquids whose kinematic viscosity is accurately known, the two constants may be evaluated.

The temperature used was 25° C., which was maintained in a water-bath kept within ± 0.01° C. The concentration of the polymer solutions ranged from 0.4 to 0.6 gm. per 100 cc. of benzene, depending on the molecular weight of the polymer. This concentration was determined for each polymer sample by evaporating 20 cc. of the solution to dryness at 70° C. In order to enable the extrapolation of the specific viscosity to zero concentration, as required for the evaluation of the intrinsic viscosity, it was necessary to determine the viscosity of each polymer sample at three different concentrations. Thus, in addition to the polymer solution prepared originally, two others were obtained from it by aliquot dilution with benzene, using dilution ratios of 1 : 1 and 1 : 3, respectively.

(*d*) *Determination of a Precipitation Distribution Function for Polymers Obtained at Different Conversions*

Since the value of a viscosity average molecular weight is so greatly dependent on the type of molecular weight distribution, it was felt that a measure of the heterogeneity of each polymer sample would be of assistance in evaluating changes in viscosity. A simple method of fractional precipitation was used for this purpose, as outlined by Wall (12). Twelve fractions of 15 cc. each of polymer solution were used to which were added 10 cc. of a mixture of various proportions of methanol and benzene. The proportions of methanol and benzene in the precipitating solutions were such that the final volume per cent of methanol in the final solution ranged from 16.7 to 33.3%. The fraction of polymer remaining in solution, denoted by f was then plotted against the volume per cent of methanol in solution, denoted by Φ, and a solubility curve thus obtained. By differentiating this solubility function, and plotting the negative slope, $-\frac{df}{d\Phi}$, against the volume per cent methanol, Φ, a precipitation distribution curve was obtained. According to Wall (12), such a precipitation distribution curve has been found to agree fairly closely with the actual molecular weight distribution existing in the polymer sample.

Results and Discussion

Rates of Polymerization and of Mercaptan Disappearance

Data on the rates of polymerization and rates of mercaptan disappearance for all the mercaptans used are shown in Tables I to IV, inclusive. It can be seen that the rates of polymerization were approximately the same in the case of the decyl, dodecyl, and hexadecyl mercaptans, amounting to an average of 6% conversion per hour up to 72% conversion. This is in agreement with the rate generally obtained for the usual GR-S polymerization. The octyl mercaptan exhibited a slightly lower rate of polymerization, i.e., about 5% per hour up to 60% conversion. It is interesting to note that, after 12 hr., the rate of polymerization dropped considerably, as shown in the

TABLE I

GR-S POLYMERIZATION WITH SHARPLES TERTIARY OCTYL MERCAPTAN

Initial mercaptan concentration = 1.5×10^{-3} moles per 100 gm. monomers

Sample No.	Polymerization time, hr.	Conversion, %	Unreacted mercaptan, %	Solubility, %	Intrinsic viscosity, [η]
13 *A*	1	4.2	21	—	—
13 *B*	2	9.2	9.5	100	0.73
13 *C*	4	19.6	2.6	100	0.83
13 *D*	6	30.8	1.3	100	1.02
13 *E*	9	47.6	—	94	1.88
13 *F*	12	66.4	—	76	1.67

$r = 13.7$; $k = 0.45$; initial mercaptan loss = 64%.

TABLE II

GR-S POLYMERIZATION WITH SHARPLES TERTIARY DECYL MERCAPTAN

Initial mercaptan concentration = 1.5×10^{-3} moles per 100 gm. monomers

Sample No.	Polymerization time, hr.	Conversion, %	Unreacted mercaptan, %	Solubility, %	Intrinsic viscosity, [η]
16 *A*	2	9.7	45	100	0.79
16 *B*	4	22.8	27	100	0.98
16 *C*	6	34.8	17	100	1.18
16 *D*	9	54.8	3.7	100	1.75
16 *E*	12	70.8	1.1	100	2.44

$r = 3.95$; $k = 0.175$; initial mercaptan loss = 33%.

TABLE III

GR-S POLYMERIZATION WITH SHARPLES TERTIARY DODECYL MERCAPTAN

Sample No.	Polymerization time, hr.	Conversion, %	Unreacted mercaptan, %	Solubility, %	Intrinsic viscosity, [η]
Initial mercaptan concentration = 1.5×10^{-3} moles per 100 gm. monomers					
11 *A*	2	13.1	64	100	0.92
11 *B*	4	25.2	44	100	1.09
11 *C*	6	36.8	30	100	1.25
11 *D*	9	58.3	5.7	100	1.74
11 *E*	12	72.2	2.0	100	2.61
Initial mercaptan concentration = 3.0×10^{-3} moles per 100 gm. monomers					
12 *A*	2	12.9	61	100	0.55
12 *B*	4	26.8	40	100	0.58
12 *C*	6	39.2	27	100	0.66
12 *D*	9	59.6	6.2	100	0.81
12 *E*	12	74.1	1.1	100	1.15

$r = 3.16$; $k = 0.02$; initial mercaptan loss = 4.5%.

TABLE IV

GR-S POLYMERIZATION WITH SHARPLES TERTIARY HEXADECYL MERCAPTAN

Sample No.	Polymerization time, hr.	Conversion, %	Unreacted mercaptan, %	Solubility, %	Intrinsic viscosity, [η]
Initial mercaptan concentration = 1.5 × 10^{-3} moles per 100 gm. monomers					
14 *A*	2	13.3	91	11	—
14 *B*	4	23.4	87	15	—
14 *C*	6	32.5	82	16	—
14 *D*	9	52 8	75	17	—
14 *E*	12	70.6	53	18	—
14 *F*	15	79.8	39	32	—
Initial mercaptan concentration = 3.0 × 10^{-3} moles per 100 gm. monomers					
15 *A*	2	13.3	95	98.6	3.59
15 *B*	4	22.5	90	76	3.62
15 *C*	6	34.6	82	59	3.69
15 *D*	9	55.0	69	58	3.27
15 *E*	12	71.8	55	65	2.80
15 *F*	15	81.5	38	69	2.53
Initial mercaptan concentration = 5 × 10^{-3} moles per 100 gm. monomers					
17 *A*	2	12.2	94	100	2.34
17 *B*	4	23.4	88	100	2.59
17 *C*	6	37.2	81	100	3.01
17 *D*	9	53.9	73	100	2.40
17 *E*	12	66.7	64	100	2.25
17 *F*	18½	86.7	26	100	2.07

r = 0.58; k = 0; initial mercaptan loss = 0.

hexadecyl mercaptan runs (Table IV). Thus in increasing the time of polymerization from 12 to 18½ hr., the conversion was increased only from about 70 to 87%.

In Fig. 1 are shown the various curves obtained when the logarithm of the per cent unreacted mercaptan is plotted against the conversion. It is evident that the rate of disappearance of the dodecyl and hexadecyl mercaptan is independent of the initial concentration. Furthermore, with the exception of C_8, all the mercaptans show a straight line up to about 40% conversion, apparently following a first-order disappearance rate up to that point. Hence it is possible to calculate a regulating index, *r*, for these mercaptans, as shown at the foot of each table. It is interesting to note that in all the cases except that of the hexadecyl mercaptan the straight line obtained at low conversions

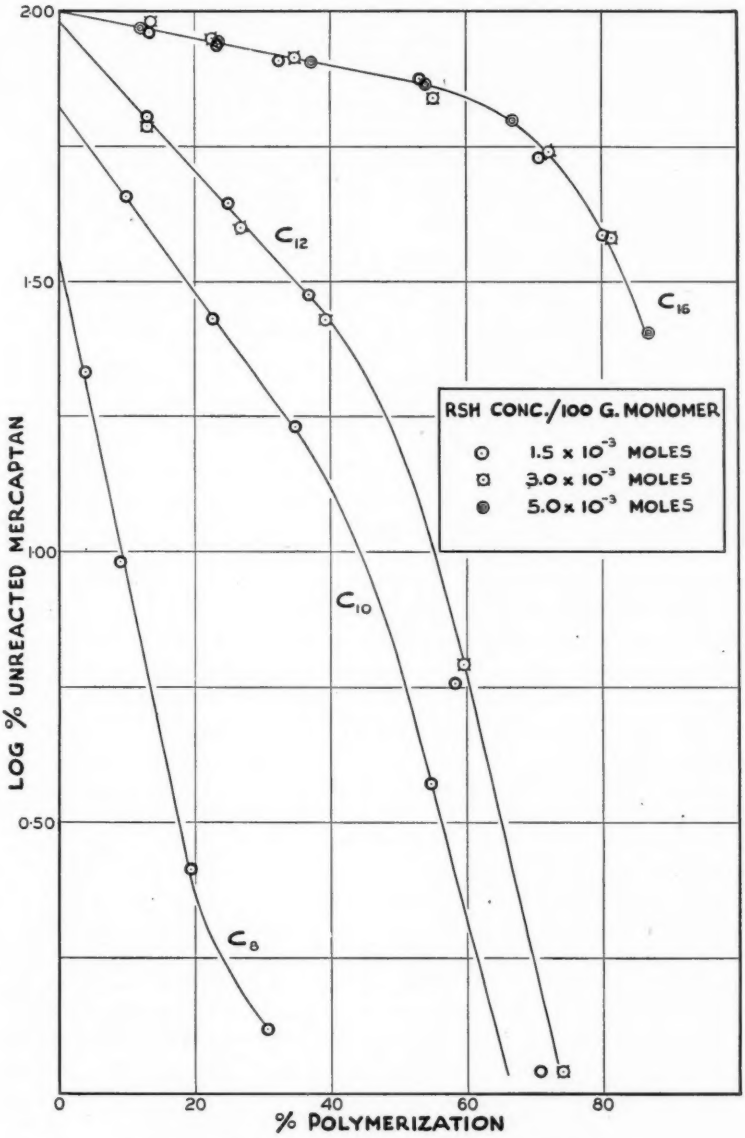

FIG. 1. *Rate of disappearance of various tertiary mercaptans.*

does not pass through the origin but has an intercept on the ordinate. Hence the equation of this straight line is expressed by

$$P = -\frac{2.3}{r}\log\frac{R}{R_0} - \frac{2.3\,k}{r} \qquad (4)$$

$$= -\frac{2.3}{r}\left[\log\frac{R}{R_0} + k\right],$$

where P is fraction of polymer formed at any given time,

R is the concentration of mercaptan at that time,

R_0 is the initial concentration of mercaptan,

r is the regulating index,

k is a constant denoted by the intercept on the $\log\frac{R}{R_0}$ axis.

This equation differs somewhat from the original equation of Ewart *et al.*, where no account is taken of the intercept on the $\log\frac{R}{R_0}$ axis, thus,

$$P = -\frac{2.3}{r}\log\frac{R}{R_0}.$$

According to Kolthoff (7) the constant, k, represents the loss of mercaptan that occurs at the beginning of the polymerization by oxidation to disulphide. This loss, according to evidence presented by Kolthoff, is known to occur entirely in the very early stages of the polymerization reaction. Hence the straight lines obtained in plotting the logarithm of unreacted mercaptan against the conversion can, on this basis, be accepted as true indications of the disappearance of mercaptan by its modifying action. If, on the other hand, the mercaptan continues to undergo side-reactions during the course of the polymerization, then the straight line obtained may be merely fortuitous. No evidence on this point, other than that offered by Kolthoff, can be presented at the present time.

As can be seen, each mercaptan has a characteristic value for r and k. Thus the regulating index of the tertiary octyl mercaptan has the high value of 13.7 while that of the hexadecyl mercaptan has the low value of 0.58. The regulating indices of the decyl and dodecyl mercaptans are fairly similar, as shown by their values of 3.95 and 3.16, respectively. In other words, the octyl mercaptan is a very active modifier and hence disappears very rapidly, the decyl and dodecyl mercaptans are not as active as the octyl, and therefore disappear more slowly, whereas the hexadecyl mercaptan is much less active and consequently disappears much more slowly. On the basis of this line of reasoning, the octyl mercaptan should yield very low molecular weight polymer at the start of the polymerization, but the molecular weight of the polymer should increase rapidly owing to the sharp decline in the mercaptan concentration. In the same way, the relatively inactive hexadecyl mercaptan should give fairly high molecular weight polymer at the start of the polymerization, and its slower rate of disappearance should, therefore, not lead to any sharp increase in molecular weight of the polymer during the course of the polymeri-

zation. These considerations will be reviewed more fully in the light of the data on the characterization of the polymers obtained at various conversions.

The value of the constant, k, deserves some discussion. For the sake of convenience, this constant has been recalculated to show its true significance, i.e., the mercaptan loss at the very start of the polymerization. It can be seen that, on this basis, the octyl mercaptan experiences a loss of 64% of its initial concentration before it starts its modifying action, the decyl mercaptan shows an initial loss of 33%, the dodecyl mercaptan shows a much smaller loss of 4.5%, while the hexadecyl mercaptan shows no loss whatsoever. It is not surprising to see a correlation between the initial loss of these mercaptans and their rate of disappearance during polymerization, since these are both functions of the reactivity of the mercaptan in question.

From the above considerations it becomes apparent that the magnitude of the constant, k, will also affect the molecular weight of the polymer formed, since it alters the effective initial concentration of mercaptan. In other words, because a large proportion of the octyl mercaptan is postulated to disappear before it has an opportunity to act as a modifier, the initial concentration of this mercaptan is in actuality much less than expected.

Hence the molecular weight of the polymer formed at the start of such a polymerization should be somewhat higher than if the octyl mercaptan had not suffered such a depletion. Stating this in another way, the molecular weight of the polymer formed is a function both of the regulating index of the mercaptan and of its initial concentration. Hence the value of k should have an important effect on the molecular weight, inasmuch as it affects the real initial concentration of the mercaptan.

Solubility and Intrinsic Viscosity of Polymers

Data on the benzene solubility and the dilute solution viscosity of the various polymers obtained with different mercaptans and at different conversions are also shown in Tables I to IV, inclusive. It can be seen that at the concentrations used, the octyl, decyl, and dodecyl mercaptans yielded soluble polymer during the greater part of the polymerization The hexadecyl mercaptan, however, when present in a concentration of 3.0×10^{-3} moles per 100 gm. of monomer, or less, showed formation of insoluble polymer even in the early stages of the reaction. This is shown in Table IV. Here the intrinsic viscosities apply only to the soluble portion of each polymer, as would be expected. The results obtained with the use of a still lower concentration of hexadecyl mercaptan viz., 1.5×10^{-3} moles per 100 gm. of monomers, are not shown in the above tables, since the resulting polymers had a very low content of soluble material, much too low for any significant viscosity data. However, since it was considered of interest to note the variation in gel formation during the course of such a polymerization, the solubility values are shown separately in Table V.

The value for the intrinsic viscosity of each polymer was derived in the usual fashion, by extrapolating to zero concentration the straight line obtained

TABLE V

SOLUBILITY OF GR-S MODIFIED BY TERTIARY HEXADECYL MERCAPTAN

1.5×10^{-3} moles mercaptan per 100 gm. monomers

Sample No.	14 *A*	14 *B*	14 *C*	14 *D*	14 *E*	14 *F*
Conversion, %	13.3	23.4	32.5	52.8	70.6	79.8
Solubility, %	11	15	16	17	18	32
Wt. of gel/100 gm. monomers	12	20	27	44	58	54
Gel swelling index	12	15	17	20	28	158

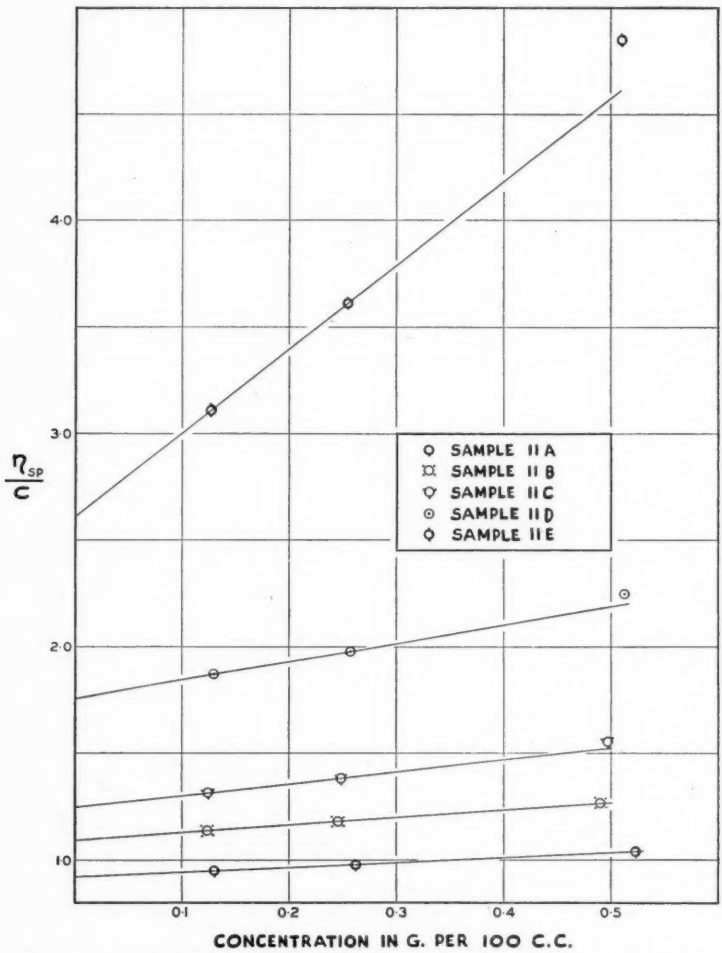

FIG. 2. *Viscosity–concentration curves of polymers modified by tertiary dodecyl mercaptan (1.5×10^{-3} moles per 100 gm. monomers).*

by plotting η_{sp}/c against c (9). A typical series of such lines is shown in Fig. 2. It may be noted that, although the polymers obtained at low conversions exhibit a good linearity between the three concentrations used, this is not so for the high conversion polymers. The latter have been found, in most cases, to yield viscosity–concentration curves having a definite concavity upwards that could not be accounted for by any experimental error. In those cases, it was assumed that the solutions of higher concentration deviated more markedly from ideality. Hence a straight line relation was assumed between the two lower concentrations, and the extrapolation carried out on that basis.

Table VI contains a summary of the relations between intrinsic viscosity, conversion, regulating index, and wastage factor of each mercaptan. The conversion figures are shown in whole numbers on the basis of the average rate of polymerization, i.e., 6% per hour during the first 12 hr. An examination of these figures shows just how each mercaptan affected the molecular size of the polymer formed. Thus the octyl mercaptan, which has a rapid rate of disappearance (high value of r), produced a polymer of relatively low molecular weight in the early stages of the polymerization; but the molecular weight of the polymer apparently increased quite rapidly during the later stages of the reaction until, at higher conversion, gel formation began owing to the depletion of modifier. It must be remembered that this mercaptan suffered a great loss by side-reaction during the very early stages of polymerization, hence its effective initial concentration was really much lower than expected. It may be assumed, therefore, that in the absence of this initial loss the intrinsic viscosity of the polymer formed at the start of the polymerization would have been much lower than indicated. This also helps

TABLE VI

INTRINSIC VISCOSITY – CONVERSION DATA ON GR-S POLYMERS USING VARIOUS MERCAPTANS

Conversion, %	Intrinsic viscosity of polymers				
	Octyl mercaptan, 1.5×10^{-3} moles per 100 gm. monomers	Decyl mercaptan, 1.5×10^{-3} moles per 100 gm. monomers	Dodecyl mercaptan		Hexadecyl mercaptan, 5.0×10^{-3} moles per 100 gm. monomers
			1.5×10^{-3} moles per 100 gm. monomers	3.0×10^{-3} moles per 100 gm. monomers	
12	0.73	0.79	0.92	0.55	2.34
24	0.83	0.98	1.09	0.58	2.59
36	1.02	1.18	1.25	0.66	3.01
54	1.88	1.75	1.74	0.81	2.40
72	—	2.44	2.61	1.15	2.25
86	—	—	—	—	2.07
Regulating index of mercaptan	13.7	3.95	3.16	3.16	0.58
Initial loss of mercaptan, %	64	33	4.5	4.5	0

to explain why the octyl mercaptan, with its high regulating index, did not produce initial polymer of very much lower viscosity than that produced by decyl or dodecyl mercaptan, when all had apparently the same initial concentration. If it were not for the extensive depletion of the octyl mercaptan at the start of the reaction, it would have been logical to expect a much greater modification of the polymer by this mercaptan as compared to the others.

This principle is demonstrated in a converse fashion in the case of the dodecyl mercaptan. Although its regulating index of 3.16 is considerably lower than that of the very active octyl mercaptan, it is still a relatively active modifier. Thus, when it was present in the usual concentration of 1.5×10^{-3} moles per 100 gm. monomers, its rate of disappearance caused a fairly rapid increase in the intrinsic viscosity of the polymer formed. However, when its initial concentration was doubled, then the intrinsic viscosity of the initial polymer was lowered considerably and the rate of increase in viscosity was much slower during the polymerization. Hence it can be seen that a modifier having a fairly high regulating index, when present in a low initial concentration, results in a polymer of great molecular heterogeneity at high conversions. If the same modifier is present in a larger initial concentration, then the resulting polymer will be more homogeneous at high conversions but the average molecular weight will be much lower. Thus a modifier with a regulating index of 3 or higher can produce either a very heterogeneous polymer of moderately high average molecular weight, or a more homogeneous polymer of much lower average molecular weight.

Although the question of the most favourable molecular weight and molecular weight distribution for synthetic rubber is still undecided, there is much indication that a polymer of high molecular weight and relative homogeneity is definitely desirable. It is obvious, then, that this can be achieved by using a modifier with a low regulating index in a suitable initial concentration to yield reasonably high molecular weight polymer at the start of the polymerization. Such a modifier would then cause only a slight increase in molecular weight during the polymerization, since its rate of disappearance would be quite slow.

In this connection, it is interesting to examine the results obtained in using the hexadecyl mercaptan at three different initial concentrations. This regulator is apparently too inactive to yield completely soluble polymer, when present in initial concentrations of 1.5×10^{-3} moles and 3.0×10^{-3} moles per 100 gm. of monomers. However, when the concentration was raised to 5.0×10^{-3} moles, completely soluble polymer was obtained at conversions up to 90%. From the intrinsic viscosities obtained using hexadecyl mercaptan at this concentration, it can be observed that the average molecular weight of the polymer showed a slow increase up to a conversion of about 40%, and then exhibited a somewhat sharper decline, which continued right up to about 90% conversion. This type of behaviour, i.e., a decreasing average molecular weight during part of the polymerization reaction, is quite different from anything encountered in the case of the other modifiers.

It may be readily noted that the increasing intrinsic viscosity occurred during that part of the polymerization reaction where the rate of disappearance of the hexadecyl mercaptan followed the first-order equation, i.e., up to 40% conversion. Thus the period during which the intrinsic viscosity decreased corresponds with the period during which the mercaptan disappearance curve showed a sharply increased rate. This phenomenon can be due to two possible mechanisms:

(1) Formation of lower molecular weight polymer during the later part of the polymerization reaction, due to an increased rate of disappearance of modifier, caused by some unknown factor.

(2) Formation of lower molecular weight polymer by interaction between the mercaptan and the polymer already present, i.e., by some mechanism of chain scission.

In this connection it is of great interest to examine the results shown in Table V. From the per cent solubility it can be seen that the total polymer, at any time during polymerization, showed an increasing solubility. This may again be due to two different effects, viz., either the formation of progressively more soluble polymer increments, or interaction between mercaptan and any insoluble polymer already formed. The calculation of the total weight of gel present per 100 gm. of original monomers is helpful in this case. It may be seen that the actual quantity of gel has suffered a reduction between the 12th and 15th hour of polymerization. In addition, it may be noted that the character of this gel has changed from that of a highly cross-linked structure ('tight gel') to that of a weakly cross-linked network ('Type A' gel), as indicated by the sharp rise in the gel swelling index. This evidence points to some bond scission reaction between the mercaptan and the gel.

It must be stated, however, that it is very probable that the rate of modification by the hexadecyl mercaptan is actually increased during the later part of the polymerization, aside from any polymer–mercaptan reaction. It is obvious that above 70% conversion, where the rate of polymerization begins to fall off, the rate of mercaptan disappearance should increase, since the original assumption of Ewart *et al.* no longer holds. However, it is equally apparent from Fig. 1 that the regulating activity begins to increase before this conversion is reached. Such an increased rate of regulating activity could possibly be due to the following effects:

(1) Change in the locus of reaction,

(2) Slow rate of solubilization of hexadecyl mercaptan,

(3) Change in butadiene–styrene ratio.

It is known that after 30 to 40% polymerization all the soap becomes adsorbed on the polymer particles and the locus of reaction shifts from the original soap micelles to the polymer particles themselves. Since this may favour an increased solubility of mercaptan it may also be the cause of an increased rate of disappearance of the mercaptan. As for the second factor mentioned above, it is known that the solubilization rate of tertiary hexadecyl mercaptan

is markedly slower than that of the lower mercaptans. Hence it is possible that, during the later part of the polymerization, when the solubility of this mercaptan shows an increase, its rate of activity would also show an apparent increase. In other words, there would arise the double effect of an increased amount of solubilized mercaptan and a decreased concentration of monomer. This possibility cannot be ignored. It is also well known that the rate of entry of butadiene and styrene into the polymer is such as to lead to an accumulation of styrene so that the composition of the polymer formed after 50 or 60% conversion changes markedly toward higher styrene content. This change may have an effect in changing the rate of regulation. It is impossible at present to state definitely which of the above factors is responsible for the anomalous behaviour of hexadecyl mercaptan during the later stages of the polymerization reaction, but it is hoped that further work will help to elucidate the mechanism.

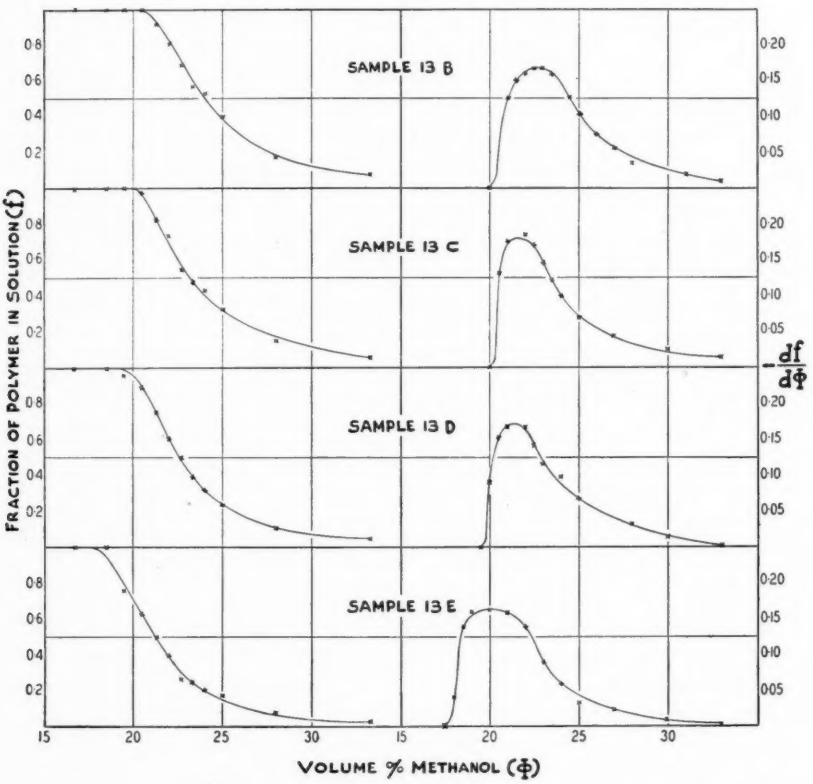

FIG. 3. *Precipitation distribution functions for polymers modified by tertiary octyl mercaptan (1.5 × 10^{-3} moles per 100 gm. monomers).*

Precipitation Distribution Functions of Polymers

The precipitation distribution functions obtained for all the completely soluble polymers are shown in Figs. 3 to 7. The solubility curves were drawn in such a fashion as to best fit the experimental points, while the distribution curves were then plotted by determining the change in slope of the solubility curves during precipitation. In this way a smooth continuous function was obtained.

It is evident from a general examination of all the precipitation distribution curves that the polymers became more molecularly heterogeneous during the

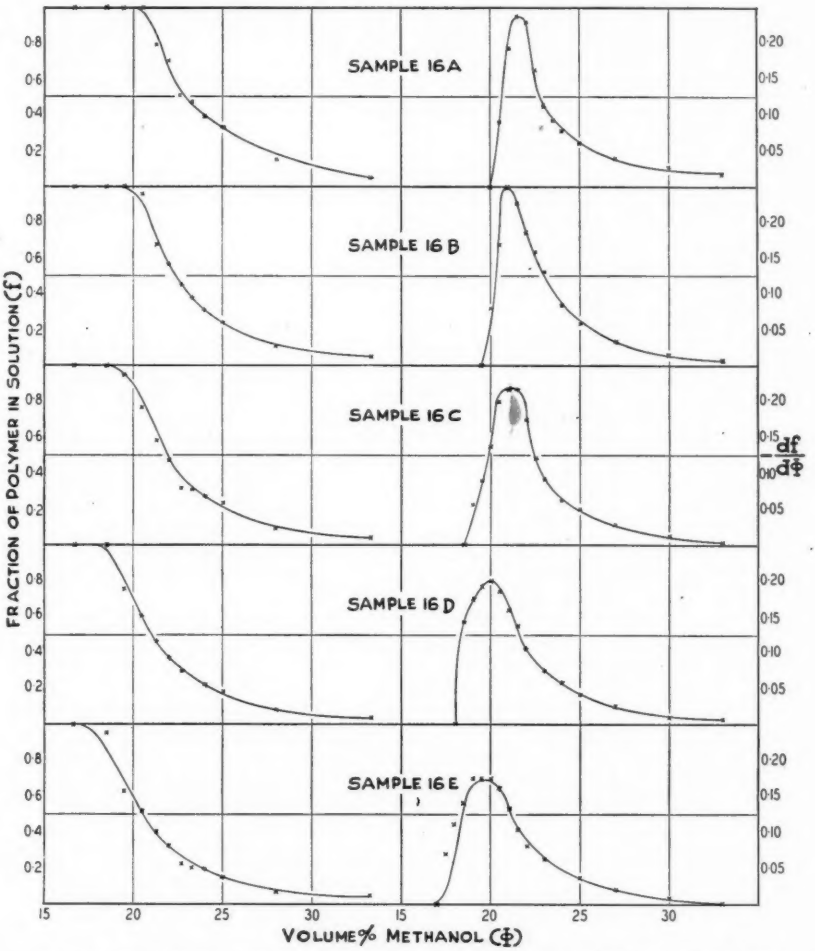

FIG. 4. *Precipitation distribution functions for polymers modified by tertiary decyl mercaptan (1.5×10^{-3} moles per 100 gm. monomers).*

course of the polymerization. However, it must be borne in mind that these curves do not necessarily represent an accurate quantitative measure of the molecular heterogeneity. Thus it can be seen that all the polymers showed a long 'tail' in the direction of the lower molecular weights and a much more abrupt slope at higher molecular weights. This is very likely an exaggerated effect caused by the high solubility of the lower molecular weight material as compared to that of the higher molecular weight polymer, and need not represent a true molecular weight distribution. From a consideration of the kinetics of addition polymerization, and from data obtained by careful

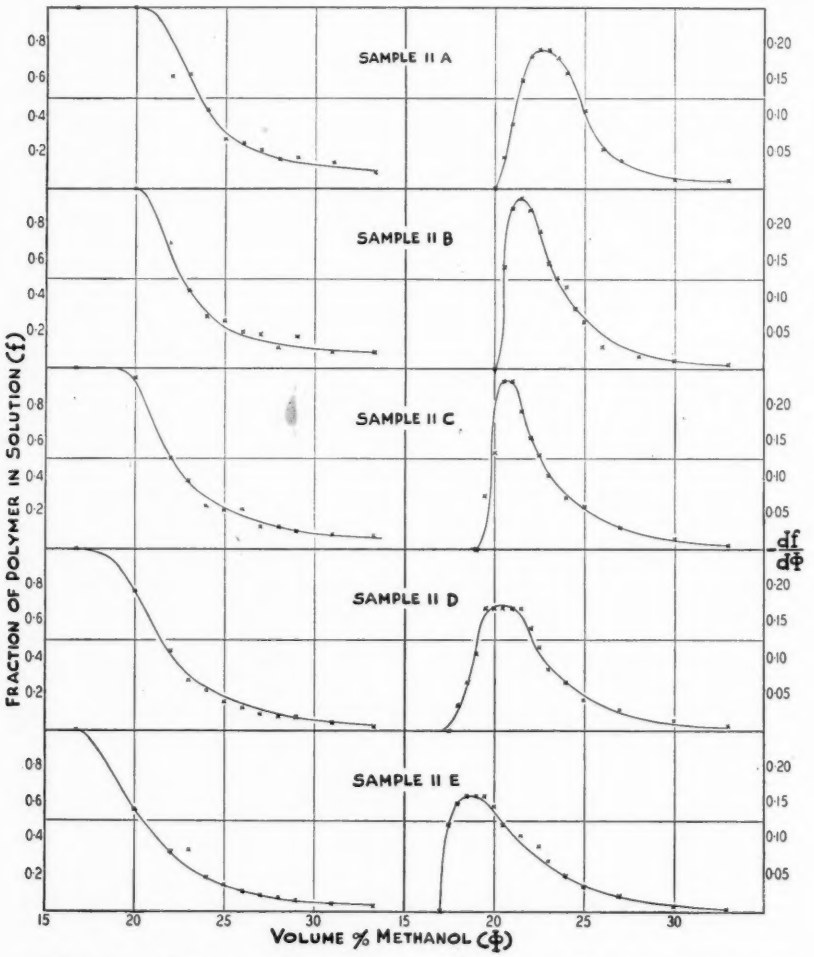

FIG. 5. *Precipitation distribution functions for polymers modified by tertiary dodecyl mercaptan (1.5 × 10⁻³ moles per 100 gm. monomers).*

fractionation studies, it has been shown that the molecular weight distribution of this type of polymer generally exhibits an abrupt rise in the low molecular weight region and an extended slope in the high molecular weight region. This is the exact reverse of the type of distribution curve shown in Figs. 3 to 7, inclusive, since increasing values of the volume per cent methanol (Φ) represent the precipitation of polymer having decreasing values of molecular weight. The fact that these precipitations were carried out with the use of only 12 precipitant solutions undoubtedly helps to decrease the accuracy of the curves. Furthermore, Flory (5) recently pointed out that in any fractionation of a

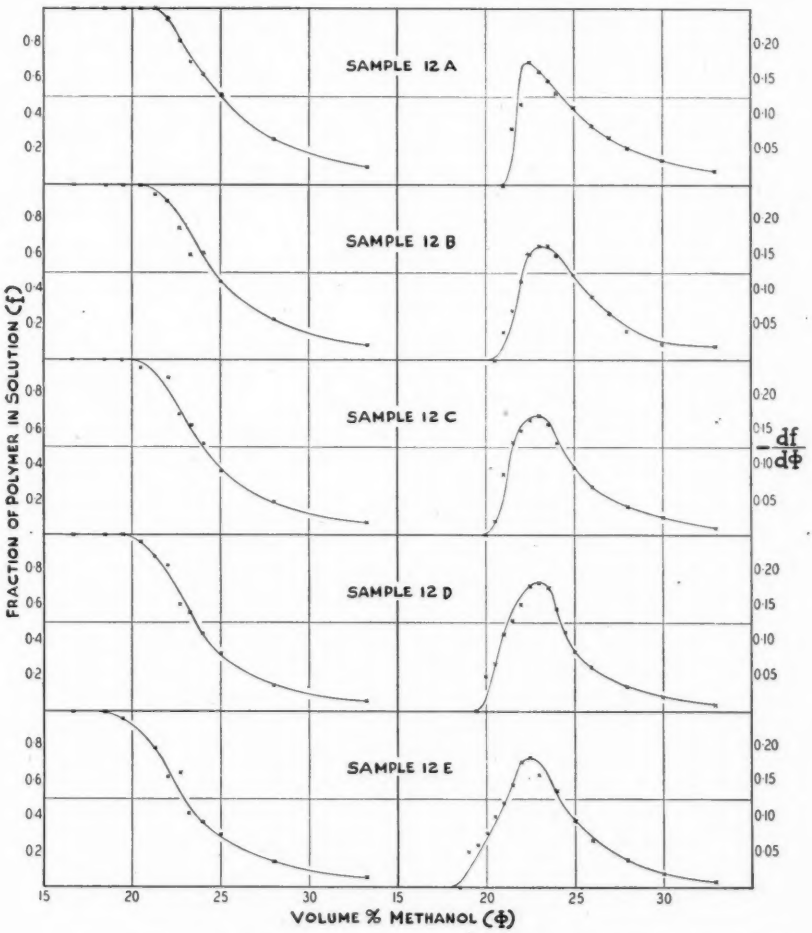

FIG. 6. *Precipitation distribution functions for polymers modified by tertiary dodecyl mercaptan (3×10^{-3} moles per 100 gm. monomers).*

polymer solution due consideration must be given to the great differences in solubility of high and of low molecular weight material, and that this must be done by adjusting the concentration of the solution for each molecular species.

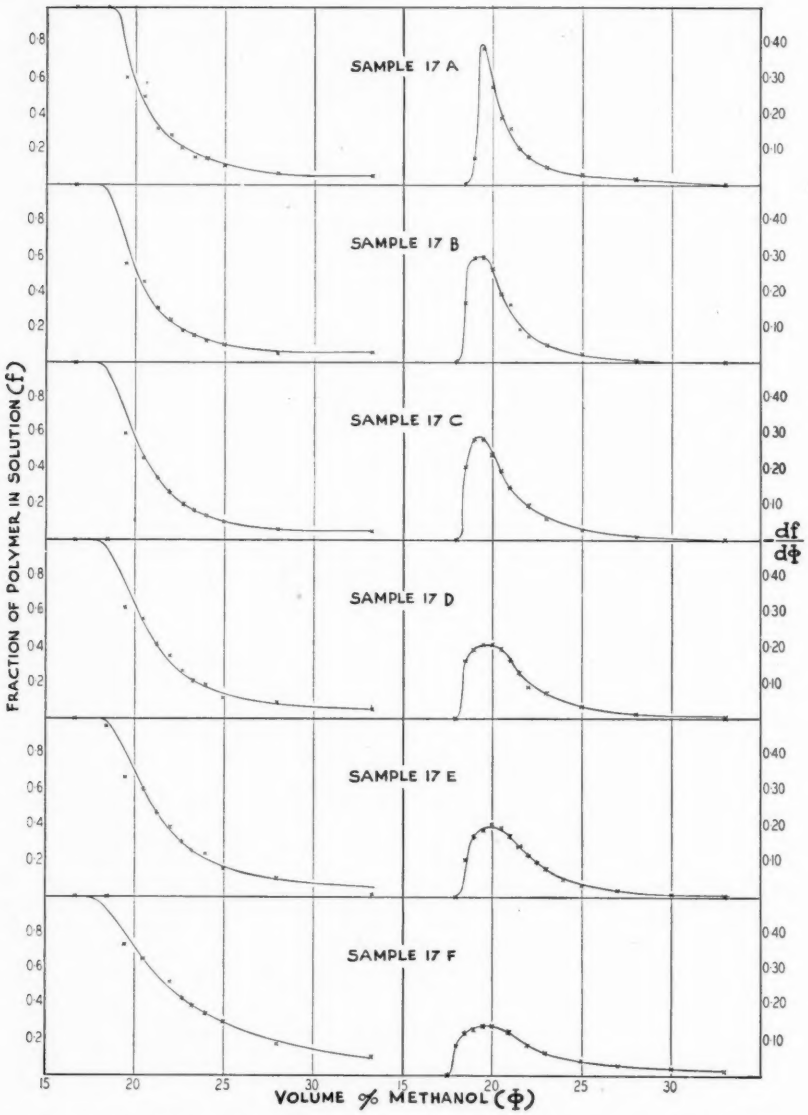

FIG. 7. *Precipitation distribution functions for polymers modified by tertiary hexadecyl mercaptan (5×10^{-3} moles per 100 gm. monomers).*

However, it can be said that the precipitation curves shown here still represent at least a qualitative picture of the molecular homogeneity of the polymers under consideration.

Although all the distribution curves undergo a shift towards higher molecular weights (lower Φ values) and, at the same time, show a wider spread, denoting increased heterogeneity, they do so in varying degrees. Thus it can be seen that the polymers modified by decyl mercaptan (Fig. 4) and dodecyl mercaptan (Fig. 5) show approximately the same degree of heterogeneity and the same change in heterogeneity during the polymerization, when both mercaptans are present in the same concentration. However, when the dodecyl mercaptan is used in a higher concentration (Fig. 6) the change in heterogeneity is not as great during the course of the polymerization. This is in agreement with the previous discussion on the relation between the regulating index and intrinsic viscosity.

Another illustration confirming the previous discussion can be seen in the curves of the polymers modified by octyl mercaptan. Here it would be expected that the change in heterogeneity would be marked during the course of the reaction, since this mercaptan has a high rate of disappearance, i.e., low molecular weight polymer should be formed at the start of the polymerization and very high molecular weight polymer during the later stages. However, it has already been noted that a large proportion of this mercaptan disappears by a side-reaction at the very start of the polymerization, hence the effective concentration is reduced drastically and thus the polymer produced initially is not as low in molecular weight as would be expected. Hence the distribution curves, as shown, do not indicate a drastic change in heterogeneity with increasing conversion. Instead they show a relatively moderate increase in heterogeneity as well as the expected shift toward higher molecular weight.

The distribution curves obtained in the case of the GR-S modified by hexadecyl mercaptan (Fig. 7) show perhaps the most interesting changes. It should be remembered that the ordinates here have been drawn to half-scale, compared to the ordinates used for all the other curves. Hence the height of each distribution curve should be doubled, for a comparison with the other polymers. The most striking feature in this series of curves is the marked increase in heterogeneity during the course of the polymerization. This increase in heterogeneity is apparently accomplished by a simultaneous increase in both the higher and lower molecular weight fractions. It can be seen that up to 40% conversion (Samples 17*A*, 17*B*, and 17*C*) there is a definite shift towards the higher molecular weights, the amount of lower molecular weight material remaining relatively constant. However, during the latter part of the polymerization (Samples 17*D*, 17*E*, 17*F*) there appears to be a definite shift towards both the higher and the lower molecular weights, resulting in a flattening and broadening of the distribution curve. This seems to confirm the postulate that there is an interaction between polymer molecules and mercaptan, occurring during the later stages of the polymerization, which leads to the formation of lower molecular weight material at the

same time as the usual chain transfer reaction continues to form higher molecular weight polymer.

Thus it may be seen that these precipitation distribution curves offer at least qualitative evidence corroborating the evidence obtained from the data on mercaptan disappearance and intrinsic viscosities. In addition, the curves for the polymers modified by hexadecyl mercaptan offer new evidence for the postulated polymer–mercaptan reaction previously advanced.

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THE EQUILIBRIUM DIAGRAMS AND CRYSTALLIZATION VELOCITIES OF THE SYSTEMS: (*a*) PICRIC ACID – 2,4-DINITROPHENOL; (*b*) DINITROPHENOL – TRINITROTOLUENE; (*c*) PICRIC ACID – DINITROPHENOL – TRINITROTOLUENE[1]

By A. N. Campbell[2] and E. J. Pritchard[3]

Abstract

The equilibrium diagrams of the systems: picric acid – 2,4-dinitrophenol, trinitrotoluene – 2,4-dinitrophenol, and picric acid – dinitrophenol – trinitrotoluene have been determined.

As this investigation was carried out to find the suitability of various mixtures for shell filling, the densities of a number of liquid mixtures of the above components were determined. For the same reason, viscosities and crystallization velocities were investigated.

The crystallization velocities were far from additive, the crystallization velocity of a mixture being less than that of either of the components. Tammann's type of curve, in which the velocity of crystallization attains a constant value after a certain degree of supercooling, was not obtained, but a maximum crystallization velocity resulted, in most cases, at about 20° to 30° C. of supercooling. Comparison of viscosity and crystallization velocity shows that a direct relation does not exist, but increase of viscosity at constant temperature does always reduce the crystallization velocity.

Addition of guncotton increased the viscosity of Shellite considerably without producing much effect on the crystallization velocity. The addition of a crystalline third component lowered both the melting point and the crystallization velocity.

Introduction*

Picric acid by itself is a violent explosive, but the pure material melts at too high a temperature (122° C.) for convenient shell filling, 105° C. being the maximum temperature permissible. It is also rather sensitive. By the addition of 2,4-dinitrophenol, the melting point of the mixture is lowered below the above maximum, and this addition also renders it much less sensitive.

During the first World War, Italy and France (6, pp. 78, 174) used a mixture of picric acid and dinitrophenol in the proportions: 65% picric acid and 35% dinitrophenol. Great Britain used a similar mixture, called 'Shellite', consisting of 60% picric acid and 40% dinitrophenol.

Although Shellite was an improvement on pure picric acid, from the point of view of shell filling, it was not completely satisfactory, because of the large amount of shrinkage on solidification. The idea was therefore put forward, by Dr. Wright of Toronto University, that the amount of cavitation might be reduced if it were possible to cool the melt to room temperature, before

[1] *Manuscript received August 9, 1946.*
Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.

[2] *Professor of Chemistry and Head of Department.*

[3] *Holder of a Bursary under the National Research Council of Canada, 1942–1943.*

* *The work described in this paper was carried out under the auspices of the National Research Council of Canada: permission to publish has now been given.*

crystallization set in. The shrinkage would thus be from the top downwards, and a further charge could then be added. The problem therefore was that of retaining Shellite in the vitreous condition, at least for a time, after it had cooled to room temperature. It has been shown by one of us (A.N.C.) (3), that, while it seems impossible to prevent the spontaneous formation of nuclei, their velocity of growth can readily be decreased by increasing the viscosity of the medium.

A systematic investigation was therefore carried out on the following characteristics of the systems mentioned in the title:

1. Equilibrium diagrams,
2. Densities of liquid mixtures at 130° C.,
3. Viscosities of liquid mixtures at 130° C.,
4. Velocities of crystallization of the pure substances and of the eutectic mixtures with increasing degrees of supercooling.

After the above data were obtained, the experiments were repeated using various addition agents to increase the viscosity and decrease the velocity of crystallization.

Previous Work on Crystallization Velocity

The literature of this subject is fairly extensive and probably fairly well known. It is sufficient to say that the classical theory of the crystallization velocity of a supercooled liquid is that of Tammann (12). According to this theory, after a certain, and rather small, degree of supercooling, the temperature prevailing at the crystallizing boundary is always the melting temperature, independent of the degree of supercooling. In accordance with this, Tammann found experimentally that the velocity of crystallization increased rapidly with degree of supercooling, to attain a constant maximum, over a large range of supercooling: this maximum value again decreased for very great degrees of supercooling. More recently, in 1929, doubt has been cast on Tammann's theory. By direct measurement, and by mathematical treatment, Pollatschek (7) showed that the temperature prevailing at the boundary, solid–supercooled liquid, was never that of the melting point. In accordance with this and Pollatschek's own results for crystallization velocity, it would appear that the velocity of crystallization should attain a maximum value and then immediately decrease, without the existence of a region of constant crystallization velocity. Our results are in agreement with this finding.

Experimental Technique

The techniques of thermometry, viscosimetry, and density are too well known to require any description. The apparatus for determining velocity of crystallization was made from thick-walled hard glass capillary of 1 to 2 mm. internal diameter. It was bent in the standard U-shape, and one arm extended into wide glass tubing to facilitate filling, and inoculation of the supercooled liquid. The length of each arm was about 12 cm. A cathetometer was used

to measure the distance crystallization had progressed downwards, in one arm, during a given time.

The first measurements of crystallization velocity were obtained by noting the time taken for crystallization to progress from one mark on the side tube to another, 10 cm. distant. This is satisfactory if spontaneous crystallization does not take place. When spontaneous crystallization does take place, it was found more satisfactory to follow the progress of crystallization from one spontaneously induced nucleus by means of the cathetometer: most of the measurements were done this way.

The determinations of equilibrium diagrams were made by two methods, viz., that of thermal analysis, accompanied whenever possible by the visual observation of the temperatures at which crystals appeared, and by the thaw point – melting point method (8, 9, 10, 11). About the former method nothing need be said, but something should be said of the latter, because it has in the opinion of the authors been somewhat neglected. The method consists simply in observing, in any melting point apparatus, the temperature at which a given mixture begins to 'thaw', i.e., to appear moist, and the temperature of complete melting, i.e., the temperature at which the last crystal skeleton disappears. In this way a complete knowledge of solidus and liquidus curves is obtained. The method requires some practice in its use, but it has the advantages that it is a semi-micro method and therefore is particularly applicable to the study of explosives and of rare and expensive substances, and, also, it occasionally gives information that cannot be obtained by the method of thermal analysis. It is also notable that the method is quite independent of supercooling, the bugbear of thermal analysis when applied to organic systems.

The drawback to the method is the necessity for very pure materials. Slight impurity causes the thaw point line to run much below the true eutectic. In this respect the method of thermal analysis does not suffer so much from slight impurity. The materials of this investigation were almost invariably commercial materials, which were not purified, and hence the results are not in agreement as regards eutectic temperatures. This criticism, however, does not apply to the determination of melting point, at least not in our technique where the rate of heating was only 1° C. in three minutes: the danger of overrunning the melting point was therefore negligible.

We used a specially designed furnace for the thaw point – melting point method, consisting of a heavy cylinder of brass with a central opening for the thermometer and melting point tube. At right angles to this central opening and at 45° to each other, two holes were drilled in the side of the cylinder. One of these served to illuminate the melting point tube, the other for observation. The source of light and a magnifiying glass to facilitate observation were mounted on the same stand. The brass cylinder was wound with two layers of nichrome wire, suitably insulated and connected in series. The temperature was controlled by means of rheostats in series with the heating

circuit. To ensure accuracy, when using the thaw point – melting point method, the temperature should not be raised more rapidly than one degree in three minutes.

Temperatures were measured by means of standardized mercury-in-glass thermometers, but were not corrected for exposed stem. All temperatures are given in degrees Centigrade. To avoid the frequent use of the lengthy names, trinitrotoluene and dinitrophenol, these are frequently abbreviated to T.N.T. and D.N.P. respectively.

Purity of Materials

The materials used throughout were the products of the explosives industry, without further purification. This was done deliberately, since the results of the investigation were intended to apply to the commercial products, and not to chemically pure material. Judging from the melting points, however, it seems that these products are not very seriously impure.

Results

Equilibrium Diagrams

1. Picric Acid – 2,4-Dinitrophenol

This system has been investigated by Bogojawlenski (2), but since the original paper was not available, we thought it advisable to redetermine the diagram. This was done both by the thaw point – melting point method and by the method of thermal analysis. The results are contained in Tables I and II (*a*). In Table II (*b*) Bogojawlenski's results are compared with ours.

TABLE I

Equilibrium data of the system: picric acid – dinitrophenol, by the thaw point – melting point method

Composition, % picric acid	Softening point, °C.	Melting point, °C.
0.0	109.0	111.5
10.0	73.7	108.0
20.0	74.8	103.2
33.4	75.0	95.6
39.6	72.5	92.7
40.4	76.2	91.6
51.1	73.1	86.7
60.0	—	82.0
60.5	74.4	82.5
61.5	75.4	83.7
69.6	74.2	93.4
80.2	72.5	105.5
88.5	72.3	111.5
100.0	119.0	121.0

2. The System: Trinitrotoluene – 2,4-Dinitrophenol

This system was investigated by the method of thermal analysis only. The results are contained in Table III.

TABLE II (*a*)

EQUILIBRIUM DATA OF THE SYSTEM: PICRIC ACID – DINITROPHENOL, BY THE METHOD OF THERMAL ANALYSIS

Composition, % picric acid	Eutectic halt, °C.	Freezing point, °C.
0.0	—	111.9
10.0	—	107.3
20.0	—	102.0
30.0	78.4	95.9
40.0	78.5	88.0
40.0	79.3	90.2
50.0	78.6	81.0
50.0	78.8	80.9
55.0	79.2	—
60.0	79.0	80.8
70.0	79.1	92.5
80.0	—	102.4
90.0	—	111.7
100.0	—	120.7

TABLE II (*b*)

THE EUTECTIC TEMPERATURE AND COMPOSITION OF THE SYSTEM: PICRIC ACID – DINITROPHENOL

Observer	Method	Melting point of eutectic, °C.	Composition, wt. % picric acid
Bogojawlenski	?	81.5	57.9
Campbell and Pritchard	Thaw point, etc.	74.0 (observed) 81.0 (from intersection of liquidus curves)	59.0
Campbell and Pritchard	Thermal analysis	79.3	56.5

3. Picric Acid – Trinitrotoluene

This system was not investigated by us, but a knowledge of it is necessary, prior to the investigation of the ternary system: picric acid – dinitrophenol – trinitrotoluene. The system had already been investigated by Taylor and Rinkenbach (13) and by Giua (5). On plotting the results of both authors, those of Taylor and Rinkenbach seem more consistent. We therefore deduced the eutectic composition and temperature from their results as 34% picric acid and 59.8° C.

4. The Systems: Picric Acid – Guncotton, and Dinitrophenol – Guncotton

The melting points of various mixtures are given in Table IV. The guncotton was incorporated in the dinitrophenol by heating it with the molten dinitrophenol for one hour at 130° C. After this time, no guncotton was detectable in the 1% mixture under the polarizing microscope, but guncotton

was still present in the form of threads in the 10% mixture. In making the guncotton – picric acid mixture, the required quantities were dissolved in acetone to secure a homogeneous mixture. The acetone was then evaporated

TABLE III

THE SYSTEM: TRINITROTOLUENE – DINITROPHENOL, BY THE METHOD OF THERMAL ANALYSIS

Composition, % D.N.P.	Eutectic halt, °C.	Freezing point, °C.
0.0	—	80.1
10.0	—	74.2
20.0	62.4	67.7
30.0	62.7	64.0
40.0	62.7	73.7 73.4
50.0	—	84.3 83.6
50.0	—	84.7
60.0	—	91.4 91.2
70.0	—	97.4 97.1
80.0	—	102.6 102.1
90.0	—	107.0
100.0	—	111.2

TABLE IV

THE EFFECT OF GUNCOTTON ON THE MELTING POINT

Composition	Melting point, °C.
D.N.P. alone	111.5
D.N.P. + 1% guncotton	112.0–112.5
D.N.P. + 10% guncotton	112.0
Picric acid alone	120.5–121.0
Picric + 5% guncotton	118–122

NOTE:—*The viscosity of the mixtures prevented accurate determinations, but it was concluded that in the concentrations of guncotton that were used there was no measurable effect.*

off, and the resulting mixture heated at 130° C. for one hour to get rid of as much acetone as possible. Although all the acetone should come off above its boiling point (56° C.), it seems to be held by the viscous guncotton solutions.

5. The System: Picric Acid – Dinitrophenol – Trinitrotoluene

The approximate ternary eutectic composition of this system was found by assuming that the binary eutectic troughs were straight and could be represented by drawing straight lines from one pure component to the opposite binary eutectic. The three lines thus drawn met in a small triangle. The mixtures corresponding to the angular points of this triangle were then prepared and investigated both by the thaw point – melting point method and the method of thermal analysis. It was found, however, that owing to the exceedingly slow growth of the crystals, the heat effect was too slowly developed to permit of the use of the latter method in its true form: instead the temperature at which crystals were first visually detectable was taken. Presumably the lowest melting of these mixtures is nearest to the ternary eutectic, but none of the three melted in a homogeneous manner. Several more mixtures in this neighbourhood were prepared, but we never obtained a mixture that melted and froze at single temperature. We considered, however, that we approached close enough to it for the exigencies of war work. All the values obtained are collected in Table V.

TABLE V

THE SYSTEM: PICRIC ACID – DINITROPHENOL – TRINITROTOLUENE

No.	Composition, wt. %			Eutectic melting, °C.	Complete melting, °C.
	Picric acid	T.N.T.	D.N.P.		
1	28	50	22	45.4	52.5
2	29	51	20	45.7 – 47.0	49.2
		Same		40.6?*	46.8
3	27	52.5	20.5	45.6	49.5
4	31	56	13	—	52.5
5	30	55	15	—	49.3
6	30	53	17	—	48.5
7	27	55	18	—	49.5
8	32	52	16	—	51.0

* *Thermal analysis for comparison.*

NOTE:—*The composition of the ternary was taken as that of No. 6: 30% picric acid, 53% trinitrotoluene, and 17% dinitrophenol. The true ternary temperature was taken as 45° to 46° C., not 48.5° C.*

6. Densities

The densities of the complete system: picric acid – dinitrophenol at 130° C. are given in Table VI (*a*) along with the equation deduced from the data by the method of averages. In Table VI (*b*), (*c*), (*d*), the densities of various other mixtures are given, determined at temperatures approximately 10° C. above the melting point. The latter data were used in the calculation of viscosities.

7. Viscosities

The viscosity and fluidity (=1/viscosity) for the system picric acid – dinitrophenol were determined and the results are given in Table VII (*a*).

TABLE VI (*a*)

DENSITY OF THE SYSTEM: PICRIC ACID – DINITROPHENOL, AT 130° C.

Composition, % picric	Density, gm./cc.	Composition, % picric	Density, gm./cc.
0.00	1.45	47.20	1.51
6.49	1.46	61.60	1.53
14.63	1.46	74.06	1.56
19.92	1.47	81.50	1.57
26.50	1.48	91.55	1.60
40.36	1.50	100.00	1.61

NOTE:—*The equation deduced from the above, by the method of averages is:*

$$D_4^{130} = 1.445 + 1.078 \times 10^{-3}p + 6.24 \times 10^{-6}p^2,$$

where D = the density, and p = weight % picric acid.

TABLE VI (*b*), (*c*), (*d*)

(*b*) Density of some mixtures of the system of Table VI (*a*) at 90° C.

Composition, % picric acid	60	55	55% plus 5% guncotton
Density, gm./cc.	1.58	1.54	1.54

(*c*) Eutectic composition of T.N.T. – D.N.P. (28% D.N.P.)

Temperature, °C., 72.8	Density, 1.47

(*d*) Density of the ternary eutectic: picric acid – D.N.P. – T.N.T.

Temperature, °C.	56.0	26.0
Density	1.54	1.56

TABLE VII (*a*)

VISCOSITY OF THE SYSTEM: PICRIC ACID–DINITROPHENOL AT 130° C.

Composition		Viscosity, centipoises	Fluidity = 1/viscosity
Wt. % picric acid	Mole % picric acid		
0.0	0.0	2.64	0.379
10.0	8.19	2.93	0.342
20.0	16.72	3.22	0.311
30.0	25.62	3.71	0.269
40.0	34.90	4.25	0.235
50.0	44.54	4.85	0.206
60.0	54.64	5.73	0.175
70.0	65.21	6.74	0.148
80.0	76.20	8.04	0.124
90.0	87.80	9.68	0.103
100.0	100.0	11.78	0.085

The viscosities of various mixtures at various temperatures are given in Table VII (*b*). In Table VII (*c*) the viscosities of the ternary eutectic for different degrees of supercooling are given.

TABLE VII (*b*)

System	Composition	Temperature, °C.	Viscosity, centipoises
Picric acid–D.N.P.	60% picric acid	90	17.96
Picric acid–D.N.P.	55% picric acid	90	15.14
Picric acid–D.N.P.	55% + 1% guncotton	90	113.7
Picric acid–D.N.P.	55% + 5% guncotton	90	Acts like glue
T.N.T.–D.N.P.	28% D.N.P.	72.8	12.96

TABLE VII (*c*)

VISCOSITY OF TERNARY EUTECTIC: PICRIC ACID – DINITROPHENOL – TRINITROTOLUENE FROM APPROXIMATELY 10 DEGREES ABOVE TO 20 DEGREES BELOW ITS MELTING POINT

Temperature, °C.	Viscosity, centipoises	Temperature, °C.	Viscosity, centipoises
56	49.3	36	180.2
51	67.4	31	290.0
46	86.5	26	470.0
41	124.2		

8. Velocity of Crystallization

Owing to spontaneous crystallization, it was found impossible to follow the velocity of crystallization of pure picric acid and pure dinitrophenol to many degrees of supercooling. The results obtained, however, agree closely with those of Bogojawlensky (1). These are given in Table VIII (*a*) and are plotted in Fig. 1.

The crystallization velocity of trinitrotoluene had not previously been determined. By following one spontaneously induced nucleus with a cathetometer, it was found possible to extend the measurements to room temperature. The results are given in Table VIII (*b*) and are plotted in Fig. 1.

The crystallization velocity of a 60% picric acid – 40% dinitrophenol mixture is given in Table VIII (*c*), and that of 55% picric acid, with 0, 1, and 3% added guncotton, is given in Table VIII (*d*), and plotted in Fig. 2, Curves I, II, and III respectively. The velocity of crystallization of the eutectic mixture in the system dinitrophenol-trinitrotoluene is given in Table VIII (*e*), while the values for the ternary eutectic are given in Table VIII (*f*). The curves of Fig. 3 refer to:— A. 60% picric acid, 40% dinitrophenol; B. 28% dinitrophenol, 72% trinitrotoluene; C. 55% picric acid, 45% dinitrophenol; D. the ternary eutectic. Curve *C* of Fig. 3 and Curve I of Fig. 2 are the same curve.

TABLE VIII (*a*)

VELOCITY OF CRYSTALLIZATION OF PICRIC ACID AND 2,4-DINITROPHENOL

Temperature, °C.	Degrees of supercooling	Velocity, mm./min.	
		Bogojawlensky	Pritchard
Picric acid			
110	12	343	366 ± 18
100	22	681	
95	27	783	
90	32	811	
85	37	858	
80	42	858	
Dinitrophenol			
100	12.8	6.35	7.52
90	22.8	16.2	18.0
80	32.8	30.3	35.4
70	42.8	55.7	
60	52.8	76.8	
50	62.8	83.2	
40	72.8	88.3	

NOTE:—*The above values are plotted in Fig. 1.*

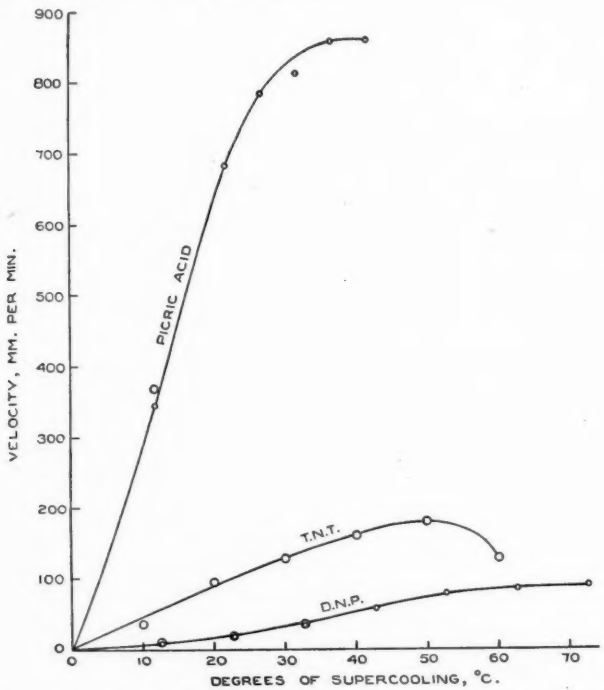

FIG. 1. *Velocity of crystallization.* o—*A. Bogojawlensky's results.* ○—*E. Pritchard's results.*

TABLE VIII (*b*)

CRYSTALLIZATION VELOCITIES OF TRINITROTOLUENE

Temperature, °C.	Degrees of supercooling	Velocity, mm./min.
22.0	58.1	127
30.0	50.1	171
40.0	40.1	158
50.0	30.1	126
60.0	20.1	94
70.0	10.1	35

NOTE:—*These values are also plotted in Fig. 1.*

TABLE VIII (*c*)

CRYSTALLIZATION VELOCITY OF THE SYSTEM: 60% PICRIC ACID – 40% DINITROPHENOL (SEE FIG. 3, CURVE *A*)

Temperature, °C.	Degrees of supercooling	Velocity, mm./min.
70	9.3	1.28
60	19.3	2.05
50	29.3	1.89
40	39.3	1.02
30	49.3	0.47
20	59.3	0.14
13	66.3	0.075

TABLE VIII (*d*)

CRYSTALLIZATION VELOCITIES OF THE SYSTEM: 55% PICRIC ACID – 45% DINITROPHENOL WITH ADDED GUNCOTTON (SEE FIG. 2 AND FIG. 3, CURVE *C*)

Temperature, °C.	Degrees of supercooling	Velocity, mm./min.		
		0% guncotton. Curve I	1% guncotton. Curve II	3% guncotton. Curve III
70	9.3	0.09	0.20	0.11
60	19.3	0.37	0.64	0.30
50	29.3	0.54	0.69	0.34
40	39.3	0.43	0.44*	0.22
30	49.3	0.23	0.38	0.13
21	58.3	0.09	0.21	0.05

* *Not plotted.*

TABLE VIII (*e*)

CRYSTALLIZATION VELOCITIES OF THE SYSTEM: 28% DINITROPHENOL – 72% TRINITROTOLUENE (SEE FIG. 3, CURVE *B*)

Temperature,° C.	Degrees of supercooling	Velocity, mm./min.
60	2.7	0.13
50	12.7	0.77
40	22.7	1.76
30	32.7	1.81

TABLE VIII (*f*)

CRYSTALLIZATION VELOCITIES OF THE TERNARY EUTECTIC: PICRIC ACID – DINITROPHENOL – TRINITROTOLUENE (SEE FIG. 3, CURVE *D*)

Temperature, °C.	Degrees supercooling	Velocity, mm./min.
36	10	0.051
26	20	0.052
0	46	0.014

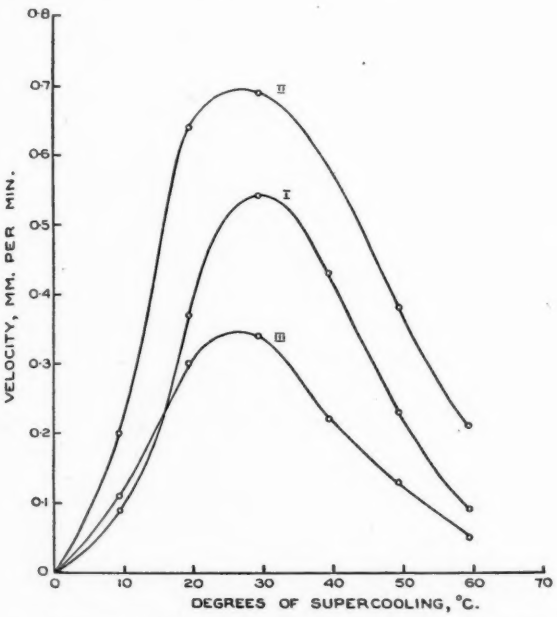

FIG. 2. *Effect on the velocity of crystallization of adding guncotton to the eutectic composition. I—Eutectic alone. II—Eutectic plus 1% guncotton. III—Eutectic plus 3% guncotton.*

Discussion of Results

Equilibrium Diagrams

The System: Picric Acid – 2,4-Dinitrophenol

Owing to the discrepancy between the results obtained for the eutectic by the two methods, no definite composition can be deduced for it. It seems, however, that the composition should be closer to 60% picric acid than 50% because the crystallization velocity of dinitrophenol is very much less than that of picric acid and therefore the method of thermal analysis tends to give results that are too low on the dinitrophenol side of the diagram. The thaw point – melting point method, however, is not affected by crystallization velocity, so that the latter method appears to be more accurate here. Comparing our results with those of Bogojawlenski, we find that his eutectic temperature (81.5° C.) is in fair agreement with ours, and probably better than ours, since it is higher, and his value for the composition of the eutectic is approximately the average of our two results. Averaging Bogojawlenski's results and our own, we arrive at the following most probable values for eutectic conditions:— composition = 57.8% picric acid, temperature = 80° C.

The System: Trinitrotoluene – Dinitrophenol

The equilibrium diagram of this system is much more satisfactory than that of picric acid – dinitrophenol. This may be due to the fact that a visual check (first appearance of crystals) was made on the thermal analysis. Although the visual method is subjective, it cannot give values that are too high, because crystals must appear before they are seen.

The System: Picric acid–Dinitrophenol – Trinitrotoluene

It was impossible to determine freezing points in this system by thermal analysis. Even the visual method was uncertain because of a natural opalescence of the melt. The composition given by us as that of the ternary eutectic may not be exact, since the thaw point and melting point did not coincide for this or any other mixture. On the other hand, this may only be due to the fact that we deliberately used the materials of the explosive industry, without further purification.

Viscosity and Velocity of Crystallization

Table VII (*a*) shows that picric acid is about 4.5 times as viscous as dinitrophenol, at the same temperature, but the velocity of crystallization is about 10 times as great as that of dinitrophenol for the same degree of supercooling. Hence the velocity of crystallization is highly characteristic, and although decreased by viscosity, the latter is not a determining factor between two different substances.

It has been observed by previous workers, as well as ourselves, that the crystallization velocity of mixtures is irregular, owing to concentration changes, but this difficulty is not met with in the case of eutectic mixtures, since there

is no concentration change during crystallization, and constant values for crystallization velocity are therefore obtained.

When picric acid and dinitrophenol are mixed, it might be expected that the crystallization velocity would lie between the values for the pure substances, as with the viscosities, but this is not so. A 60% picric acid mixture, which might be expected to have a crystallization velocity higher than that of pure dinitrophenol, is actually found to possess a crystallization velocity only 1/85: the temperatures are not strictly comparable, but the difference is too great to be accounted for on this basis. The cause of this is perhaps to be found in the tendency of the molecules of dinitrophenol to interfere with the formation of the crystal lattice of picric acid, and conversely.

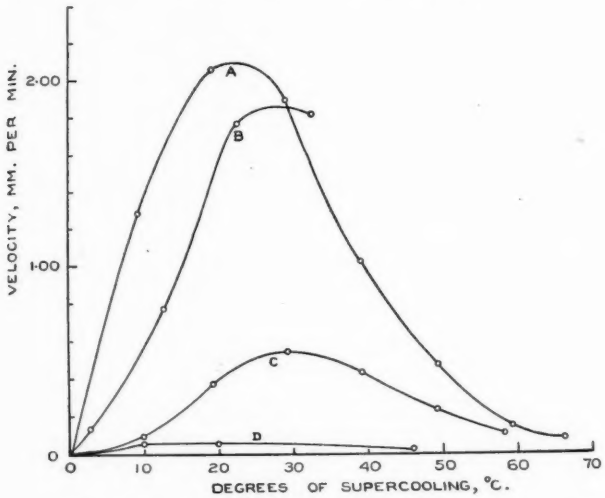

FIG. 3. *Velocity of crystallization of two- and three-component systems.*
A—60% picric acid : 40% dinitrophenol
B—28% dinitrophenol : 72% trinitrotoluene
C—55% picric acid : 45% dinitrophenol
D—Ternary eutectic.

The concentration of the second component, however, does have an effect on crystallization velocity, as would be expected, e.g., a mixture containing 60% picric acid (Shellite) has a maximum crystallization velocity of almost four times that of a 55% mixture. The crystallization velocity seems to depend on whether the mixture lies on one or the other side of the eutectic composition. If, instead of 60% picric acid, a 55% mixture had been used, Shellite would have crystallized much less readily.

By adding 1% guncotton to the 55% picric acid mixture, the viscosity is increased about 8 times, but the crystallization velocity increases about 1.2 times. This is explained by the work of Freundlich and Oppenheimer (4), who showed that non-spherical colloidal particles increased the crystallization

velocity. Since the molecule of guncotton is probably long chain, and of colloidal dimensions, the increase is accounted for. Three per cent of guncotton increases the viscosity beyond the measurable limit (30 poises), without reducing the crystallization velocity very much. The effect of increased viscosity at constant temperature is, of course, always to reduce the crystallization velocity.

An examination of Fig. 3 shows that the two component systems have crystallization velocities higher than that of the three component system made from them. This is no doubt due to some extent to the fact that the ternary system, which melts at a lower temperature than any of the component binaries, probably has a higher viscosity than any of the binaries, but this effect is insufficient to account for the very great decrease in crystallization velocity. It seems a general rule that the crystallization velocity of mixtures is lower than those of the components, quite apart from considerations of viscosity.

None of our curves expressing velocity of crystallization as a function of supercooling show a region of constant velocity of crystallization, as in Tammann's experimental work. A maximum value is attained, at 20° to 30° C. of supercooling, which then rapidly decreases.

General Conclusion

The purely practical, war-time problem, viz., that of obtaining an explosive containing picric acid which should remain for a long time in the vitreous state has been only partially solved. We did indeed obtain a mixture, containing picric acid, dinitrophenol, and trinitrotoluene, which would remain in the liquid state at room temperature and crystallize only very slowly, but the melting point of this mixture is too low for a shell filling. Interesting data on crystallization velocity have, however, been incidentally obtained. It will be shown in a subsequent paper that the problem is practically solved by the use of a Shellite containing picramide.

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